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Structure and Bonding

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Preface

The fullerene family represents a new molecular form of pure carbon, which has proven to be of remarkable interest for both its chemical and physical properties. Following the serendipitous discovery of $C_{60}$ (a quasi-spherical molecule with dimensions of ~ 1 nm) and the production of bulk crystalline samples of fullerenes from arc-processed carbon, research on the solid-state properties of fullerene-based nanostructures and nanonetworks has proceeded at an exhilarating pace. Novel carbon materials like the nanotubes, the buckyonions and the endohedral metallofullerenes have been subsequently discovered, while fullerene derivatives show a plethora of interesting properties, ranging from superconductivity to ferromagnetism and promise future applications in batteries, transistors, solar cells and sensors among others. The present volume contains contributions from both theorists and experimentalists and attempts to highlight some of the interdisciplinary issues, presently at the forefront of fullerene research. I hope the reader will benefit from the range of topics covered in this volume and find the issues stimulating and possibly able to generate new ideas and approaches to these fascinating materials.

I warmly thank all the authors who enthusiastically contributed their outstanding work for this volume.

Brighton, January 2004

Kosmas Prassides
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Organofullerene Materials

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Abstract The most significant developments of recent years on organofullerene materials are presented in this comprehensive review. With selected examples chosen from the current literature, original and well-established synthetic protocols utilizing mainly addition and cycloaddition reactions that have been successfully applied to fullerenes, are discussed. Among these, 1,3-dipolar cycloadditions, Bingel cyclopropanations, and various [2+2], [3+2], and [4+2] cycloadditions are the most useful reactions and have been widely applied for the construction of novel organofullerene materials. Emphasis is also given to the applications of these materials in diverse fields varying from nano- to biotechnological areas, and from the construction of plastic solar cells and optical limiting glasses to DNA photocleavage, magnetic resonance imaging (MRI) agents, and quantum computing.

Keywords Fullerenes · Materials · Applications · Nanotechnology · Biotechnology
1 Introduction

An important field of organic chemical investigation emerged soon after the remarkable discovery [1] and macroscopic production [2, 3] of fullerenes, a new allotrope form of carbon after diamond and graphite. As by definition organic chemistry deals with the chemistry of carbon, the progress in this field by exploring fullerene organic transformations was rapid. Twelve years after the first isolation and preparation of synthetically useful amounts of fullerenes, the exohedral covalent functionalization of C₆₀ is continuing unabated. The main advantage gained upon functionalization of fullerenes is the solubility enhancement of the so-produced organofullerene derivatives. The difficult processibility of fullerenes due to their poor solubility in most organic solvents is surmounted with the aid of functionalization and the construction of novel organofullerene materials. Therefore, organic functionalization of fullerenes puts them in pole position in the run for applying envisioned innovative uses.

In general, C₆₀ is the most abundant, least expensive and therefore, most thoroughly studied member of these all-carbon hollow-cluster materials. The overall fullerene structures can be imagined as fused 1,3,5-cyclohexatrienes and [5]radialenes, with alternation of single and double bonds. The latter are located exclusively between two six-membered rings (6,6-bonds) with a bond length of 1.38 Å, while the bonds between five- and six-membered rings (5,6-bonds) are essentially single with a length of 1.45 Å. The energy cost for introducing one double bond between a five- and a six-membered ring has been calculated as approximately 8.5 kcal mol⁻¹ [4]. In addition, a large amount of strain energy exists within the cage due to the highly pyramidalized sp² hybridized carbon atoms [5]. The substantial curvature of fullerenes is reflected by an average sp².278 and a fractional s-character of the p-orbitals of 0.085 [6]. A closed-shell electronic configuration for C₆₀ consisting of 60 π-electrons [7] gives rise to a completely full HOMO (highest occupied molecular orbital) that is energetically located approximately 1.8 eV lower than the corresponding antibonding LUMO (lowest unoccupied molecular orbital)[7–9]. Both the threefold degeneracy and low energy possession of this LUMO make C₆₀ a fairly good electron acceptor with the ability of reversibly gaining up to six electrons upon reduction [10, 11], either in the solid state or in solution. Furthermore, the solubility of the electrogenerated species is highly increased as compared with neutral C₆₀.
As a result, the following rules regarding the chemical reactivity mainly of C\textsubscript{60}, and to a lesser extent to the rest of the family of fullerenes, can be deduced:

1. C\textsubscript{60} chemically behaves as an electron-deficient polyalkene, with rather localized double bonds. Thus, the reactions that mainly take place involve cycloadditions, additions of nucleophiles, free radicals, and carbenes, as well as \( \eta^2 \)-complexation with various transition metal elements.

2. The relief of strain in the fullerene cage is the primary driving force for addition reactions, by altering the hybridization of the reacting fullerene carbon atoms from a trigonal sp\textsuperscript{2} to a less strained tetrahedral sp\textsuperscript{3} configuration.

3. The regiochemistry of the addition reactions is governed by the minimization of the 5,6-double bonds within the fullerene skeleton. Therefore, any 1,2-addition reactions produce ring-closed 6,6-adducts having two sp\textsuperscript{3} carbon atoms on the fullerene framework. However, sometimes ring-opened 6,5-adducts (fulleroids) are formed, keeping all fullerene carbon atoms sp\textsuperscript{2} hybridized.

Several original and well-established synthetic protocols, in combination with the plethora of chemical reactions that have been successfully applied mainly to C\textsubscript{60}, have established this novel form of carbon as a useful building block in organic synthesis. Fundamentally, it is the combination of the unique structural, physicochemical, and electronic properties of fullerenes with the special characteristics of the added groups that eventually leads to the development of new materials with enormous potential in fascinating and widespread technological and biological applications. A wide variety of organofullerene materials have been specifically designed and successfully synthesized providing promising applications in diverse nano- and biotechnological areas, such as electronic and optoelectronic devices, light emitting diodes (LED) and photovoltaics, thermotropic liquid crystals, sensors, storage media, and microfabrication, as well as DNA photocleavage, HIV protease inhibition, photodynamic cancer therapy, and nuclear medicine. This chapter highlights the rapid progress made in the above scientific areas by the synthesis and applications of some novel organofullerene materials.

### 2 Fulleropyrrolidine Materials

Azomethine ylides are organic 1,3-dipoles possessing a carbanion next to an immonium ion [12]. Cycloadditions to dipolarophiles provide access to pyrrolidine derivatives, useful intermediates in organic synthesis with stereo- and regiochemical control. Azomethine ylides can be readily produced upon decarboxylation of immonium salts derived from the condensation of \( \alpha \)-amino acids with aldehydes or ketones. When they are added to C\textsubscript{60}, a fulleropyrrolidine monoadduct is formed in which a pyrrolidine ring is fused to the junction between two six-membered rings of a fullerene [13–15]. Very importantly, functionalized aldehydes lead to the formation of 2-substituted fulleropyrrolidines, whereas reaction with N-substituted glycines leads to N-substituted fulleropyrrolidines (Scheme 1).

The combination of the characteristics of the fullerene skeleton with the fused pyrrolidine ring is of great importance for the construction and synthesis of materials with novel properties. The most attractive feature of fulleropyrrolidines is
their easy preparation, with many possible synthetic variations. Structurally different derivatives can be obtained by either using properly functionalized azomethine ylides or by modifying a fulleropyrrolidine intermediate. Both ways have led to a wide variety of compounds specifically designed for diverse biological and technological applications that are discussed in the appropriate following sections.

Finally, modifications of this type of addition have resulted in introducing fused heterocyclic rings other than pyrrolidine on fullerenes. Thus, the tetrahydrofuran ring was fused via the intermediate formation of carbonyl ylides and their subsequent addition to C$_{60}$ [15], while in a similar fashion, thiocarbonyl ylides have been used to fuse thiophene rings with fullerenes [16, 17].

3 Methanofullerene Materials

Besides the 1,3-dipolar cycloaddition of azomethine ylides to C$_{60}$, the Bingel cyclopropanation reaction is widely used for regioselective functionalization of fullerenes. In principle, this versatile modification involves the generation of carbon nucleophiles from $\alpha$-halo esters and their subsequent addition to C$_{60}$ [19]. The addition takes place exclusively on double bonds between two six-membered rings of the fullerene skeleton, yielding methanofullerenes. As shown in Scheme 2, addition of diethylbromomalonate to C$_{60}$, in the presence of an auxiliary base
such as NaH or DBU, leads to methanofullerene possessing two carboxy groups attached to the bridging sp³ carbon atom.

The novelty of this type of organic functionalization is explained in terms of the wide number of different methanofullerene materials that can be reached due to the presence of esters moieties: either properly functionalized carbon nucleophiles can be constructed that ultimately would add to C₆₀, or additional chemical transformation to the addend group of an already synthesized methanofullerene could occur. Thus, theoretically, any chemical group carrying novel physical, electronic, magnetic, or mechanical properties that fulfills the appropriate requirements for the construction of novel organofullerene hybrid materials can be properly designed and, thus, attached on the fullerene skeleton.

In recent years, modifications of the original Bingel reaction have appeared. In those modifications, novel strategies utilizing (i) carbanionic precursors to methanofullerenes other than malonates, and (ii) alternative pathways generating the reactive monohalomalonate intermediate in situ [20], have been developed. As a subsequent result, the potential of applications of such types of organic functionalization for designing and constructing new organofullerene materials has been significantly increased.

Bromoketoesters, bromoketones, and even malonic acid monoesters have been used in modified Bingel reactions, as precursors, to synthesize methanofullerene materials [19, 21]. Furthermore, a series of phosphonium [22] and sulfur [23] ylides have been reacted with C₆₀ following a similar addition–elimination pathway, yielding the corresponding methanofullerenes. However, the yields of the latter reactions can be varied significantly, from 10% for some phosphonium ylides to 40% for some sulfur ylides, depending on the nature of the ylide used. In a recent promising application, a methanofullerene material having a formyl group at the bridgehead carbon was reported [24]. The novelty of such a functionalized material arose upon the ready conversion of the free formyl group to a variety of N-arylaldimines and explained in terms that can be used for the construction of efficient acceptor–donor dyad systems.

In another example, (C₆₀)₂ dimer was used for a Bingel reaction [25]. In this work, cyclopropanation with diethyl malonate in the presence of an auxiliary base was conducted on (C₆₀)₂ to yield a mixture of monoadducts. The monoaddition reaction can be considered as “bisfunctionalization” of one of the C₆₀ cages and this explains the formation of isomers. The same reaction was also carried out on dimeric material encapsulating ³He in one of the C₆₀ cages. However, that functionalization was more complicated with regio-isomeric products arising from addends either on an empty C₆₀ cage or a ³He-encapsulating one.

An important field where the cyclopropanation reaction finds growing application is the construction of dendrimers possessing fullerenes either as functional cores [26–33] or branches [34–38]. Dendrimers can serve as building blocks for the construction of organized materials with nanosize precision due to the well-defined three-dimensional structure they possess. An issue of great importance is to incorporate photoactive and/or redox-active units at the center of the dendrimer in order to establish these types of materials as molecular devices. An example of an organofullerene material that has the potential to serve as a core building block for the construction of dendrimeric compounds...
(as well as a precursor to \(C_{2v}\)-symmetrical pentakis adducts) has been recently synthesized. Thus, utilizing the Bingel cyclopropanation reaction under template activation conditions, a highly symmetrical decaakis adduct of \((C_{60})_2\) was produced [39].

Several cyclopropanated organofullerene materials have been synthesized for the preparation of fullerene-containing thermotropic liquid crystals. A wide variety of such liquid-crystalline materials were synthesized possessing mono- [40–42], hexa-addition [43] pattern, or even dendritic addends [44–46].

Equally important to Bingel functionalization of fullerenes has been the observation that reduction of such formed adducts with two electrons causes rapid methanofullerene ring opening and reverse Michael-type addition, to yield starting fullerene as product [47]. Thus, the retro-Bingel reaction has allowed fullerene-cyclopropanated adducts to serve as protecting groups for further chemical transformations. The latter consideration has already been applied for the preparation of pure enantiomers of the higher fullerene \(C_{76}\), as well as symmetrical bis-methano adducts of \(C_{2v}\)-symmetrical \(C_{78}\) and pure \(C_{2v−C_{78}}\) [48].

4 Cycloadded Organofullerene Materials

Among other suitable ways for synthesizing stable and fairly soluble organofullerene materials are cycloaddition reactions. Either thermal or photochemical cycloadditions have been performed producing a wide variety of cycloadded organofullerene materials, due to the remarkable property of fullerenes to function as \(2\pi\) electron-deficient dienophiles and dipolarophiles. Furthermore, cycloadditions can give different products depending on the reaction phase (solution or solid state). In this context, \([2+2]\), \([3+2]\), and \([4+2]\) are the most widely used reactions to form cycloadducts, with the diene always added to the 6,6 double bonds of the fullerene skeleton. Due to the stability of the cycloadducts, further side-chain functionalization can be applied for the construction of intriguing materials.

4.1 \([2+2]\) Cycloadditions

Cyclobutanefullerenes (four-membered rings fused to 6,6 junctions) are typically formed upon \([2+2]\) cycloadditions. Basically these types of cycloadditions are less common, with the first reported example being the thermal \([2+2]\) cycloaddition of benzyne to \(C_{60}\) [49, 50].

Schuster and co-workers [51–54] reported photochemical \([2+2]\) cycloadditions of cyclic enones and 1,3-diones to \(C_{60}\), while Cheng [55] reported the addition of electron-poor alkenes. The interesting points of these works can be summarized as follows: (i) these photocycloadditions can’t proceed at irradiations where only \(C_{60}\) absorbs light (i.e., 532 nm); and (ii) the product yields are increased either by decreasing the concentration of fullerene or by increasing the concentration of enone. These findings led the authors to conclude that \(^2C_{60}\) does not undergo addition to the ground state of the enones but, instead, the enone triplet excited state adds to the fullerene ground state via an intermediate triplet 1,4-biradical.
In another mechanistic study, Foote and co-workers reported a possible charge-transfer mechanism for the photochemical [2+2] cycloadditions of electron-rich ynamines [56–58]. Further studies on the regio- and stereoselectivity upon addition of less electron-rich substrates such as alkyl-substituted 1,3-butaedienes [59], acyclic enones [60], and aryl alkenes [61] to C_{60} were performed in more recent years.

Addition of diethylaminopropyne to C_{60} resulted in a [2+2] cycloadduct that can be ring-opened under acidic conditions, while, when followed by oxidative cyclization in the presence of activated carbon, novel fullerene lactones were formed [62]. Further work on the reaction of C_{60} with propiolates in the presence of triphenylphosphine resulted in the construction of bismethanofullerenes and a [2+2] cycloadduct consisting of a cyclobutane ring fused to a 6,6 ring junction [63].

Recently the scientific interest regarding all-carbon fullerene dimers has increased [64]. The unique physical properties of fullerene dimers provide intriguing possibilities as model compounds for nanotechnological and polymer science and offer potential access to novel electronic devices. Komatsu and co-workers applied mechanochemical conditions for the solid-state synthesis of several [2+2] dimeric fullerene structures. In their first report, C_{60} was dimerized in the solid state utilizing the so-called technique of high-speed vibrating milling (HSVM), in the presence of potassium cyanide [65, 66], while the same reaction in solution only affords C_{60}-cyanated derivatives [67]. In another application of the HSVM technique, the reaction of C_{60} with pentacene in the solid state afforded the corresponding 2:1 adduct [68], instead of the 1:1 cycloadduct that is
formed in solution [69]. In an independent study of such [2+2] cycloadditions, the solid-state dimerization of the higher fullerene C_{70} [70] was reported as well as the synthesis of cross-dimers C_{60}–C_{70} [71].

Due to the higher reactivity of the C–C bonds at the poles of the C_{70} molecule that have the highest π-bond orders, they are exclusively involved in the above mentioned dimerizations–cycloadditions. Therefore, five [2+2] addition isomers of (C_{70})_{2} and two of the cross-dimers (C_{60})(C_{70}) were formed that were finally resolved in the pure forms with the aid of recycling high-pressure liquid chromatography (HPLC). In all these all-carbon dimers (Scheme 3), the [2+2] connecting bonds can be easily cleaved under electroreductive conditions, suggesting that such kinds of dimeric materials can be used as prototypes in molecular switches based on fullerene architectures.

4.2 [3+2] Cycloadditions

Five-membered rings fused to 6,6 junctions are formed upon [3+2] cycloadditions to fullerenes. A wide variety of such systems have been prepared with the majority involving heterocyclic structures. However, the most popular system involving such cycloadditions is the 1,3-dipolar addition of azomethine ylides leading to fulleropyrrolidines. Additional examples utilizing that methodology can also be found in the following sections discussing novel technological applications for the construction of donor–acceptor hybrid systems.

Among other examples, the thermal [3+2] cycloaddition of azides to C_{60} [72–74] plays a role in the initial step towards the macroscopic synthesis of [60]azafullerenes [75–77]. 1,3-Dipolar cycloaddition of azides to C_{60} at temperatures below 80 °C occurs preferentially to a 6,6 double bond affording the corresponding thermally labile triazolines. Due to the lower symmetry D_{5h} of C_{70} as compared to I_{h} symmetrical C_{60}, the regiochemistry of [3+2] cycloadditions of azides gives isomeric mixtures of [70]triazolines (Scheme 4) that can be eventually separated and serve as precursors in the synthetic route to [70] azafullerenes [79–81].

In another example, diazo compounds cycloadd to fullerenes across a 6,6 double bond to give fulleropyrrozolines, that decompose to mixtures of methanofullerenes and methanofulleroids either thermally or photochemically [82].

Finally, buta-2,3-dienoates and buta-2-ynoates, in the presence of phosphine as catalyst, have been found to react with C_{60} in a [3+2] fashion [83, 84], contrary to the earlier observations of yielding [2+2] cycloadducts [85].
4.3 [4+2] Cycloadditions

In the classical [4+2] Diels–Alder cycloaddition reaction, 1,3-dienes add to fullerenes to form cyclohexene rings fused to 6,6 junctions. Again, this type of cycloaddition offers the great advantage of controlling the degree as well as the site of addition. The several examples of such cycloadditions reported so far in the literature can be roughly divided into two main categories: (i) those in which the 1,3-dienes are cycloadded directly to the fullerene skeleton and (ii) those in which the 1,3-dienes are generated in situ from the reactants.

As far as the first category of reactions is concerned, a nice and representative example deals with the addition of several analogs of Danishefsky dienes to give the functionalized fullerene-fused cyclohexanones [86], as shown in Scheme 5. The presence of the carbonyl group makes this system suitable for further chemical transformations, leading to useful materials in nanotechnological areas.

The second category of [4+2] cycloadditions has been applied in order to construct novel organofullerene materials possessing fused furan and thiophene rings [87,88], suitable for nanoelectronics and photovoltaics applications. Other examples of such cycloadditions involve reactive quinodimethane species created in situ by thermolysis of cyclic sulfones [89], substituted cyclo- [89,90] or benzocyclobutanes [91], and 1,4-elimination of dibromides [91].

Recently, the reaction of “masked” ortho-benzoquinone [92] with C₆₀ was tested [93]. The [4+2] cycloaddition reaction of such electron-deficient dienes with fullerenes resulted in the formation of highly functionalized bicyclo[2.2.2]octenone-fused fullerenes. The reactants were generated in situ by the oxidation of the readily available 2-methoxy phenols with hypervalent iodine agents. For the several different masked ortho-benzoquinones that were tested, it was found that the yield of the cycloadducts depends on the nature of the starting materials and the reaction conditions. Other Diels–Alder reactions of such electron-deficient dienes with electron-poor fullerenes involved tropones [94], 1,3-butadienes substituted with electron-withdrawing groups [95], and 2-pyrone [96].

Heterocyclic analogs of ortho-quinodimethane have become increasingly popular for Diels–Alder functionalization of C₆₀. Several methods for generating these highly reactive species have been developed; however, most attention has been paid to their generation via chelotropic elimination of SO₂ from het-
eroaromatic-fused 3-sulfolenes and 1,4 elimination from the corresponding $\alpha,\alpha'$-dihalides [97–101].

Solid-state reaction of condensed aromatic compounds such as anthracenes, tetracene, pentacene, and naptho[2,3-$a$]pyrene with C$_{60}$ under HSVM conditions has also been applied, to yield the corresponding [4+2] cycloadducts [102]. Although the reaction with anthracene afforded the same product (in better yields) than the one when the reaction was carried out in solution [103–105], with pentacene it gave an adduct that could not be obtained in solution conditions, in which a pentacene unit was attached to two C$_{60}$ molecules. Furthermore, reaction with tetracene and naptho[2,3-$a$]pyrene afforded the expected [4+2] cycloadducts, similar to the case when the reactions were carried out in solution.

It should be noted that all the work described and cited in this section refers to monoaddition of diene to a single 6,6 ring junction of fullerenes. By using an excess of fullerene the amount of multiadducts is minimized, while by using an excess of diene the formation of such multiadducts can be increased. In fact, the latter has been described by the synthesis of a hexakis adduct of organofullerene, upon cycloaddition of 2,3-dimethyl-1,3-butadiene to C$_{60}$ [106, 107].

Some novel C$_{60}$-based assemblies were recently synthesized by [4+2] Diels–Alder cycloaddition reactions. Thus, fused tetrathiafulvalene-C$_{60}$ dyads and C$_{60}$-tetraphiafulvalene-C$_{60}$ dumbbell triads, in which the fullerene acceptor is doubly tethered to the donor tetrathiafulvalene through a rigidified cyclohexene ring [108], were prepared. With this novel approach, control of the relative orientation as well as the distance between the donor and acceptor units was achieved. Thereby, through-space interactions were expected to dominate because of the special topology of the constructed molecules. More examples of such donor–acceptor hybrid systems are discussed in the appropriate following sections, with their potential use in innovative technological applications.

Finally, there have also been described a few examples of [4+2] cycloaddition to higher fullerenes that lead to isomeric mixtures due to their lower molecular symmetry. These involved cycloaddition of in situ-created reactive ortho-quinodimethane to C$_{70}$ and C$_{76}$ [109, 110], as well as pentamethylcyclopentadiene [111] to C$_{70}$.

5 Miscellaneous Organofullerene Materials

Beyond the widely used synthetic methodologies of 1,3-dipolar cycloadditions, Bingel cyclopropanations, and various other cycloadditions on fullerene skeletons, several novel organofullerene materials have been produced utilizing reactions that do not fall into any of the above-mentioned categories. Nevertheless, due to their unique formation, that could not otherwise be reached via those “established” synthetic methodologies, a few such chemical transformations of fullerenes are presented in this section.

A remarkable one-step five-fold addition of alkylcopper reagents to the [5] radialene structure of C$_{60}$ has generated cyclopentadienes, R$_5$HC$_{60}$, and cyclopentadienides, R$_5$C$_{60}^-$, in a novel Grignard-type fashion [112–115]. In addition, strategies for the installation of different alkyl groups have been recently devel-
oped [116]. Furthermore, secondary amines have been found to undergo a similar one-step five-fold addition to C$_{60}$ under photochemical aerobic conditions to produce tetra-aminofullerene epoxides [117] (Scheme 6).

In another example, the simple fullerene diols C$_{60}$(OH)$_2$ and C$_{70}$(OH)$_2$ have been synthesized by addition of RuO$_4$ followed by acid hydrolysis [118]. The advantage of the method was the low level of hydroxylation, and thus the prospect that these materials could ultimately serve as precursors for the construction of more complicated organofullerene derivatives.

Although it is very well established that C$_{60}$ generally behaves as an electron-deficient olefin and undergoes a variety of nucleophilic additions, it has also been shown that C$_{60}$ can undergo protonation and nitration (electrophilic additions) [119–121]. Furthermore, stable radical-cations of organofullerenes have been prepared, isolated, and studied. Such studies involved electrophilic additions of polychloroalkanes to C$_{60}$ with the simultaneous observation of monoalkyl fullerenyl cation intermediate species [122, 123]. Also, independent studies have proven the formation and full characterization of carbocations of organofullerene species; when the organofullerene derivative C$_{60}$Ar$_5$Cl [124, 125] was treated with the strong Lewis acid AlCl$_3$, carbocation species such as C$_{60}$Ar$_5^+$ were formed [126]. According to these results, a great potential utility of electrophilic additions to fullerenes is anticipated for the construction of novel organofullerene materials [127].

Finally, in recent years, great efforts have been directed towards the development of suitable synthetic methodologies for the construction of an effective aperture on the fullerene surface [128–130]. This would allow a more systematic investigation of the internal space of the all-carbon closed-cage fullerene materials. In a novel approach, following an original sequence of reactions, four bonds of C$_{60}$ were eventually cleaved, thus creating the largest orifice so far on C$_{60}$ [131]. Interestingly, incorporation of He and H$_2$ gases was successful [132], providing the basic background for the realization of an efficient synthetic approach towards the preparation of endohedral fullerenes.
6 Functionalized Endohedral Metallofullerene Materials

Endohedral metallofullerenes [133] – fullerenes encapsulating atomic or molecular species – have captured the interest of scientists because of their exciting structural, electronic, and magnetic properties as well as the possibility of applications in nanotechnology, biomedicine, or even quantum computing. The expectation that endohedral metallofullerenes will become, in the near future, an important nanostructured material for nanoscale electronic devices is explained in terms of their energy band gaps that can be varied between 1.0 and 0.2 eV depending on the fullerene size, as well as the kind and the number of the encapsulated metal atom(s).

Typically, endohedral metallofullerenes are produced in an electric arc by evaporating composite carbon rods filled with atomic or molecular elements that later end up inside the carbon cages. However, the yield of endohedral metallofullerenes is rather low, less than 1%, and their formation mechanism is unknown. Furthermore, no particular rules are applied on the selection of the carbon cage that will be formed and on the nature of the element that ultimately will be encapsulated.

There exists an intriguing challenge to disclose how the reactivity of empty fullerenes is modified upon endohedral metal doping. In 1995, the very first example of functionalized endohedral metallofullerene was reported [134]. As substrate, the metallofullerene La@C_{82}, one of the most abundantly produced endohedral metallofullerenes, was chosen. Either photochemical or thermal addition of disilirane afforded the corresponding exohedral adducts [134, 135]. The high thermal reactivity of La@C_{82} towards disilirane could be rationalized in terms of its stronger electron donor and acceptor properties compared to the empty fullerenes C_{60} and C_{70} [136], that only thermally react with disilirane. The ESR spectra measured during the reaction revealed the formation of, at most, two regioisomers with a different La isotropic splitting. Apparently, regioselectivity as well as reactivity of empty fullerenes could be controlled to a great extent by endohedral metal encapsulation.

Since then, several studies on the chemical reactivity of endohedral metallofullerenes have been performed in order to understand their basic chemical properties. The endohedral metallofullerenes Gd@C_{82} [137], La_2@C_{80}, and Sc_2@C_{84} [138] showed similar behavior towards disilirane, forming the corresponding adducts via C–Si bonds. Also, similar functionalization of La@C_{82} was achieved with digerimane [139, 140]. However, when diphenyl diazomethane was added to La@C_{82} an exohedral adduct was formed via C–C bonds [140, 141]. This organic functionalization of endohedral metallofullerenes opened the way to chemically tune the electronic properties of the so-produced materials, the degree of charge transfer, and ultimately their electronic properties.

The first Diels–Alder cycloaddition on endohedral metallofullerenes was recently reported. Sc_3N@C_{80} endohedral metallofullerene was reacted with the diene precursor 6,7-dimethoxyisochroman-3-one to yield the corresponding adduct [142], while its structure was also verified by X-ray diffraction measurements [143].
In another recent report, a novel perfluoroalkylated endohedral metallofullerene of La@C\textsubscript{82} was photochemically obtained upon reaction with perfluoroocetyl iodide (Scheme 7) [144]. During this reaction, the outer sphere of La@C\textsubscript{82} was perfluoroalkylated by utilizing a fluorous synthesis–partitioning protocol. In this approach, the perfluorinated segment for the labeling of the endohedral metallofullerenes was chosen to be large enough to force partitioning of the resulting adducts from the organic to the fluorous phase. Because of their unique physical and chemical properties, such perfluoroalkylated endohedral metallofullerene materials are capable of finding new areas of application. The high solubility of oxygen, carbon dioxide, and nitric oxide in perfluorocarbon solvents could probably direct such kinds of materials towards novel medical applications. Especially, great efforts are directed in such a way to achieve solubilization of endohedral metallofullerene materials in physiological media, including water for potential use in biotechnology.
7 Technological Applications

7.1 Plastic Solar Cells (Photovoltaics)

Fullerenes possess high electron affinity, and therefore, they have been considered to form charge-transfer complexes with weak electron donors such as conjugated polymers. It was rapidly realized that this kind of charge-transfer process occurs with composites of fullerenes and conjugated polymers. However, when these composite materials are photoexcited (when both fullerenes and conjugated polymers are better acceptors and donors, respectively) the electron-transfer process becomes more efficient. Thus, fullerene-based plastic solar cells (photodiodes) have been prepared. In the first pioneering example of such studies, when $C_{60}$ was added to polyphenylenevinylene (PPV), electron transfer occurred from the excited state of the polymer to $C_{60}$ and it was studied by photophysical and ESR means [145]. More importantly, it was found that the charge-separated state lived long enough to allow charges to migrate to the anode and cathode, and thus the first fullerene-based photodiode was constructed [146]. However, the effective interaction between the electron donor and acceptor moieties was limited to the flat geometrical interface, was rather incompatible with the spherical shape of $C_{60}$ and therefore resulted in low short-circuit photocurrent density. To overcome this difficulty, properly functionalized fullerenes were considered, and indeed showed that photodiodes fabricated from such composites could produce improved photoconversion [147–150].

Recently, an alternative elegant design for the construction of composite materials with even more promising properties as plastic solar cells has emerged. By mixing a soluble conjugated polymer (donor) and a functionalized fullerene (acceptor), the effective interaction between the two components takes place in the entire volume of the device, enhancing the generation of the photocurrent circuit [151]. Thus, current studies on such “bulk heterojunction” systems are directed towards the synthesis of conjugated polymer backbones (donor cables) bearing directly grafted or tethered fullerene moieties (acceptor cables). Not only can both the electronic and morphological properties of the composite materials be controlled, but also, more importantly, the secondary structure of the macro-molecule could be dictated by its primary structure (double-cable polymer). Furthermore, the interaction between the donor-conjugated backbone and the acceptor moieties may be tuned by varying the chemical structure of their connecting fragment [152]. In such double-cable polymer systems, it is expected that holes should migrate away from electrons preventing recombination. Therefore, double-cable polymers appear very intriguing materials that may retain the favorable electronic and photophysical properties of conjugated polymer–fullerene composites but, very importantly, in which phase separation and clustering phenomena cannot occur.

Diverse strategies that ultimately would improve the processibility of functionalized fullerene materials and obtain their intimate mixing with conjugated polymers have been proposed. In more detail, the following systems have already
been designed and tested to a great extent as useful photodiodes: (i) diblock copolymers (i.e., conjugated donor block polymer plus fullerene-bearing block) [153]; and (ii) conjugated oligomer–fullerene dyads with different conjugation length of the donor moiety [154–161].

The majority of the synthetic studies towards the construction of novel photodiodes of fullerene-based double-cable polymers concern either electropolymerization of suitable aromatic monomeric units or copolymerization of two monomeric units, one carrying the fullerene moiety and one designed to improve solubility. Most of the electropolymerized conjugated polymeric materials bearing fullerenes that have been obtained consist of bithiophene units with low oxidation potential that favor electropolymerization [162–164]. On the other hand, the preparation of some photodiodes based on novel chemically synthesized double-cable polymers was recently reported and studied using their photophysical properties [165–170]. For example, the structures of some conjugated-backbone hybrids covalently linked with organofullerene moieties are shown in Scheme 8.

Novel hybrid materials have been realized in which fullerenes participate in composite films with $\pi$-conjugated-polymer electron donors such as oligothiophenes. Established studies have already shown that the photoinduced electron transfer is rather enhanced between $\pi$-conjugated polymers and fullerenes, while back electron transfer is considerably slower [145, 149, 171, 172]. Electrosynthesized polythiophene with pendant fullerene substituents was recently obtained from the corresponding biothiophene–fulleropyrrolidine dyad [173]. The novel material described has the potential of a double-cable polymer, heavily loaded with fullerene electron-conducting moieties.

Studies dealing with the incorporation of $\pi$-conjugated oligomeric units in fullerene dyad systems have increased, especially after the observation of electron transfer from conducting oligomers (or polymers) to $C_{60}$ [145, 174]. Some further examples on such materials involved the construction of organofullerene materials in which two oligo-phenylenevinylene [175] or two oligo-thienylenevinylene [176] units, respectively, have been attached on the skeleton of $C_{60}$ via a fused pyrrolidine ring. Further works utilizing oligo-phenylenevinylene [177, 178] and oligo-naphthylenevinylene [179–181] in fullerene hybrid systems have been performed, and found to possess intriguing physicochemical properties including singlet–singlet energy transfer as well as intramolecular electron-transfer interactions.

7.2 Donor–Acceptor Systems

Fullerenes are very good electron acceptor materials. Particularly, the most intriguing characteristics of $C_{60}$ in electron-transfer processes have been found to be its low reorganization energy and the acceleration of photoinduced charge separation. Novel applications that have been envisioned include energy storage devices, conversion of light into electric current, and mimicking natural photosynthesis [182–187]. The electron-transfer process can be controlled by covalently linking donor and acceptor moieties incorporating fullerene units. In addition,
Scheme 8
it has already been shown that the rates of forward and back electron transfer in such hybrid systems strongly depend on the molecular topology [188, 189]. In other words, the extent and the rate of charge recombination could be decreased by modulating the separation (or the spatial orientation) of the donor and acceptor units by means of flexible or rigid hydrocarbon chains or even steroid bridges, while maintaining a high rate of charge separation.

Several organofullerene donor–acceptor molecular material hybrid systems have been synthesized via 1,3-dipolar cycloaddition reactions of azomethine ylides, via Bingel cyclopropanation and methanofullerene formation intermediates as well as via cycloaddition reactions, that have already been discussed in previous sections. The majority of such hybrid systems possess always as acceptor unit the fullerene core and as donor moieties porphyrins, tetrathiafulvalenes, ferrocenes, quinones, or electron-rich aromatic compounds that absorb visible light [190–193]. The most active research topic in this particularly technological field relies (i) on the arrangement of several redox-active building blocks in

![Scheme 8 (continued)]
which multistep electron transfer can occur, (ii) the design of supramolecular systems of noncovalently attached chromophores, and (iii) the enhancement of the electron-acceptor properties of the hybrid material [194, 195].

7.2.1 Porphyrins

Photoinduced electron transfer generally takes place easily in fullerene–porphyrin hybrid systems. Attention has been paid to the construction of rigidly linked systems in which the porphyrin and fullerene units are in enforced close proximity [195–198] or are forced apart [199–202]. Representative examples of dyads, where flexible linkers allow the porphyrin unit to approach really close to the fullerene moiety, include strapped “parachute” hybrids that have been synthesized via Bingel reaction conditions [195–198]. On the other hand, steroid linkers used in independent studies were designed to provide a rigid polycyclic spacer capable of separating covalently linked donor (Ru-bipy complex or porphyrins) and acceptor (fullerene) systems well beyond the range of the van der Waals contact [199–202]. The synthesis of the latter systems was performed following the methodology of 1,3-dipolar cycloaddition of azomethine ylides to C_{60}. Interestingly, the above-mentioned dyads were obtained as diastereomeric mixtures due to the spiro-junction that connects the fulleropyrrolidine with the porphyrin unit. Consistent with the mechanism of addition, increased conjugation in the steroid unit decreased the yield and the facility of the fulleropyrrolidine intermediate.

Some representative examples of fullerene–porphyrin dyads are shown in Scheme 9. In other examples, porphyrin analogs such as phthalocyanines and subphthalocyanines have been used for the construction of efficient dyads. Again, the most straightforward approach for their synthesis involved 1,3-dipolar cycloaddition of the appropriate azomethine ylides to C_{60} [203–205]. Also, with the aid of the Bingel reaction, other phthalocyanine–fullerene systems have been prepared [206, 207] with the most prominent example being the one that contains a flexible linker possessing an azacrown subunit [208]. The novelty of this dyad can be found in the nature of the linker that could, in principle, induce conformational changes in the multicomponent system when certain ions (e.g., alkaline ions) are present. As a direct consequence this would potentially allow an external control over the electronic interactions between the phthalocyanine and fullerene units.

Recently, a novel approach for probing proximity effects in this type of dyad by using an axial ligand coordination-controlled “tail-on” and “tail-off” binding mechanism was reported [209]. The donor–acceptor proximity has been controlled either by temperature or by an axial ligand replacement and is illustrated in Scheme 10.

In another elegant work, it was shown that an electron-transfer switch could be made by linking to porphyrin an auxiliary photochromic unit that could be isomerized between a short-wavelength-absorbing form (incapable of affecting the porphyrin excited state) and a long-wavelength-absorbing form. The latter would be capable of accepting the excitation energy from the porphyrin and therefore of quenching the porphyrin-initiated electron transfer to the acceptor unit (fullerene) [210, 211].
Scheme 9
Computational studies followed by molecular modeling were performed on a variety of fullerene–porphyrin dyads that contained either flexible polyether or rigid steroid linkers as well as on doubly linked cyclophane-like C_{60}-porphyrin [212]. Not surprisingly those studies confirmed that the attractive van der Waals interactions between porphyrin and C_{60} units cause these dyads to adopt unusual conformations in order to get together in close proximity.

There is also substantial interest in studying such hybrid systems where the donor and acceptor moieties are not covalently bonded but interact with each other via supramolecular arrangements. Such supramolecular configurations of fullerene–porphyrin dyads can be achieved primarily by van der Waals interactions and then by various other factors such as electrostatic interactions, charge transfer, coordination, and solvation effects [213–217]. Importantly it should be mentioned that this type of recognition between fullerene–porphyrins differs from traditional π-π stacking interactions by the closeness of the approach and the surprising affinity of a curved molecular surface (fullerene) to a planar surface (porphyrin) [218]. It is anticipated that further studies of such systems would be important in order to manipulate photophysical properties and adjust the charge-transfer processes.

In a supramolecular approach to fullerene–porphyrin hybrids, the assembly of a rigidly connected dyad, in which a zinc tetraphenylporphyrin, Zn(TPP), is noncovalently linked to a C_{60} derivative via axial pyridine coordination to the metal, was reported [219–222]. Photoexcitation of the dyad Zn-complex led to electron transfer with very long lifetimes of the charge-separated pairs, as revealed by optical spectroscopy and confirmed by time-resolved electron paramagnetic resonance spectroscopy. Accordingly, two different solvent-dependent pathways can be considered for the electron-transfer processes. Either the excitation of the porphyrin chromophore is followed by fast intramolecular electron transfer inside the complex, or alternatively the free porphyrin is excited undergoing intermolecular electron transfer when the acceptor molecules ap-
proach closely enough during the molecular diffusion. Similar fulleropyrrolidine complexes, also including covalently linked porphyrins, have been reported [209, 221, 222].

Readers specialized in that field of supramolecular recognition between fullerenes and porphyrins can find further intriguing studies and results in the recent literature [223–233].

7.2.2 Tetrathiafulvalenes

The first synthesis of C\textsubscript{60}-based donor–acceptor dyad materials, via 1,3-dipolar cycloaddition of the appropriate azomethine ylides, bearing tetrathiafulvalene units as donor [234, 235], followed the more sophisticated approach of dyads having tetrathiafulvalene moieties highly conjugated with para-quinodimethane units linked to the C\textsubscript{60} skeleton [236]. The idea for synthesizing such \( \pi \)-conjugated tetrathiafulvalenes stems from their ability to form stable dication species which result in charge-transfer complexes with electrical and magnetic properties, in sharp contrast with simple tetrathiafulvalenes that are known to form only stable radical cations [237–239]. Therefore, not surprisingly, the former dyads showed no charge transfer in solution, while interestingly in the latter dyads magnetic measurements indicated paramagnetic behavior and remarkable conductivity. Furthermore, their redox properties were studied by cyclic voltammetry and revealed the presence of four reduction waves corresponding to the C\textsubscript{60} framework and a two-electron simple oxidation wave due to the \( \pi \)-extended donor system of tetrathiafulvalene [236].

However, in the previous systems no electronic interactions between the donor–acceptor units were observed [240]. An explanation for this could be the large separation distance between the active redox centers and the flexible bridging they share. Thus, in order to promote such interactions, a different consideration was adopted in which the linkage between C\textsubscript{60} and tetrathiafulvalenes should be via a rigid bridge. Therefore, the redox units were attached via two rigid \( \sigma \)-bonds forming a cyclohexene ring [241, 242]. That kind of bridge was proven to be very efficient for mediating in electron and energy transfer between the active units of the system by a through-bond coupling mechanism, irrespective of its length. Some novel structures of such tetrathiafulvalene dyad materials are presented in Scheme 11.

Recently, in another synthetic approach for the construction of efficient fullerene–tetrathiafulvalene dyads, a fullerotriazoline dyad (fullerotriazolines are thermally labile intermediates that are formed upon reaction of fullerenes with azides [243]) possessing a substituted tetrathiafulvalene functionality was reported [244].

In addition to the previously described donor–acceptor hybrid dyad systems, a few triads have also been considered and constructed. The fundamentals and principles for designing such triad systems are more complex, as there exist diverse arrangement options for their construction. Thus, the multiple electroactive units of a triad can be arranged in different ways giving rise to different materials [245].
Novel triads that contained tetrathiafulvalenes as electron donors and porphyrin chromophores (refer to previous section for porphyrin–fullerene dyads) as donor units have been recently reported [246] (Scheme 12). Improved analogs of the latter triads were soon considered by connecting the tetrathiafulvalene unit to a \( \pi \)-extended conjugated network [247].

### 7.2.3 Ferrocenes

Ferrocene is composed of a pair of 6-\( \pi \)-electron carbon arrays and a 6-\( d \)-electron iron(II) atom. Ferrocene–fullerene donor–acceptor dyads carry all the requisites for electron-transfer phenomena. However, data for the formation of ferrocene–fullerene hybrids are not abundant. Some such dyads have already been synthesized following the methodology of 1,3-dipolar cycloaddition of the appropriate azomethine ylides to \( C_{60} \), with either variable-spacing building blocks or a rigid-bridge all-\( \sigma \)-bonded framework, in order to tune the redox properties of the system [40, 234, 248–251]. Another novel dyad that contained two covalently bound ferrocene units was recently synthesized via cyclopropanation of the fullerene core [252].

In a very recent elegant work, the construction of a novel dyad has been described by the use of suitably modified fullerene derivatives that can serve as 6-\( \pi \)-electron donor ligands to the 6-\( d \)-electron iron(II) atom [253]. It was shown that the hybrid material could not only be oxidized reversibly like fer-
rocene itself but could also be reduced reversibly like fullerenes. In Scheme 13 some of the above-mentioned ferrocene–organofullerene dyad materials are shown.

Some more complicated hybrid systems have also been constructed, sharing more than one donor unit. In one of them, a nonlinear triad where all the electroactive units are linked to the same functionality of a pyrrolidine group (e.g., utilized the 1,3-dipolar cycloaddition of the appropriate azomethine ylides as the critical step for connecting the donor units to the fullerene skeleton) was considered [245]. With this arrangement the formation of any bisadducts was minimized.

7.2.4 Miscellaneous Hybrids

Apart from hybrid systems in which porphyrins, phthalocyanines, tetrathiafulvalenes, and ferrocenes were used as donor components, a few other electrofunctional groups have also been incorporated and considered for the construction of efficient electroactive systems. Also interestingly, oligothiophene–fullerene dyads possessing a terminal-free thiol group are ideal candidates for being assembled on gold electrodes for efficient photocurrent generation. Not surprisingly, this was the case when a novel fullerene–oligothiophene dyad possessing a tripod-dal rigid anchor was constructed [254]. In addition, fullerene–azathiophene
dyads have been synthesized following the 1,3-dipolar cycloaddition of azomethine ylides to $C_{60}$ [255, 256].

Also, a series of triads containing porphyrins as donors and various oligothiophenes as spacer units to $C_{60}$ have been also considered and synthesized. These systems have allowed the study of long-range electron transfer and aided the evaluation of its distance dependence [257].

Electron acceptors, such as 11,11,12,12-tetracyanoanthraquinodimethane (TCAQ) and its 9,10-anthraquinone (AQ) precursor have been also attached to fulleropyrrolidinle materials, since they are good candidates for obtaining fullerene-based electroactive hybrid systems [245, 258, 259].
Finally, in a novel application, some uniquely structured hexapyrrolidine derivatives of $C_{60}$ with $T_h$ and $D_3$ molecular symmetries have been synthesized and characterized by analytical methods and x-ray crystallography [260]. This work revealed strong luminescence, indicative of photophysical properties that are unusual in comparison with other fullerene derivatives. Therefore, the hexapyrrolidine adduct was utilized as a chromophore in the fabrication of a white light organic LED [261].
7.3 Optical Limiting

The π-electron delocalized system of fullerenes plays a crucial role in the existence of unusual and novel photophysical properties of these materials. As has been reported since the early stages of fullerene research, the electronic absorption spectrum of C<sub>60</sub> shows a strong absorbance in the UV region while a very weak one exists in the visible regime \([262]\). Upon organic functionalization the electronic absorption spectrum of mono-organofullerene adducts is altered, especially in the visible region, while the onset of the absorption continues down to the near-IR (in sharp contrast with pristine C<sub>60</sub> that does not absorb in the near-IR region).

Optical limiting is by definition an optical nonlinear phenomenon that results in an increase of the optical absorption as the incident irradiation increases. Due to the fact that the triplet photoexcited state of C<sub>60</sub> can absorb light more efficiently than its ground state, as the intensity of the incoming irradiation increases the intensity of the transmitted irradiation does not increase linearly \([263, 264]\). The latter, together with both the extension of optical absorption to the near-IR of mono-organofullerene adducts and the resulting reduction of symmetry of the functionalized materials, as compared with the intact C<sub>60</sub>, has allowed several
research groups to envision optical limiting applications for functionalized organofullerene materials [265].

The synthesis of fulleropyrrolidines specifically derivatized with a silicon alkoxide group and their incorporation into glassy matrices prepared via sol–gel processing has given rise to a new field of fullerene technology (Scheme 15) [266]. In principle, silicon-functionalized derivatives can be homogeneously dispersed into the final glass through covalent bonding to the oxide matrix, thus preventing aggregation of the fullerene spheroids [267–270].

A fulleropyrrolidine derivative has been synthesized and covalently linked to HPLC silica gel and the resultant material was used to separate calixarenes, cyclodextrins, and protected peptides [271]. Another type of organofullerene material containing polysiloxane was recently synthesized. It was found to be suitable for separating high-boiling-point compounds, and can be found applications as the stationary phase in capillary gas chromatography [272].

8 Biotechnological and Medicinal Applications

8.1 Empty Fullerenes

Organofullerene materials have shown great potential in a wide variety of biological activities such as DNA photocleavage, HIV-protease inhibition, neuroprotection, and apoptosis [273–275]. Since the first report that C\textsubscript{60} derivatives could be inhibitors of HIV-1 protease [276], several models have been proposed to justify that, and numerous organofullerene derivatives synthesized for such a reason [277–281]. The main considerations for the preparation of such derivatives are (i) the strategic design of novel groups in certain positions of the cage that can give electrostatic and/or hydrogen bonds with the amino-acid residues that catalyze the substrate, and (ii) the incorporation of polar groups in order to render the desired organofullerene material water soluble.

To act as photoactive agents and in order to be selectively delivered to their biological targets, fullerenes must be conjugated with molecules possessing biological affinity to certain nucleic acids, proteins, cell types, organelles, etc. On the other hand, fullerenes themselves could facilitate the interactions of certain biologically active molecules with lipophilic membranes of living cells and consequently improve cellular uptake due to their high hydrophobicity. Recently, the synthesis of a functionalized fullerene having a DNA minor groove binder and an oligonucleotide chain covalently linked to the cage via 1,3-dipolar cycloaddition of the appropriate azomethine ylides was reported [282–284]. The design of the latter synthesis was based on an already established idea that coupling of fullerenes to a minor groove binder leads to higher affinity and specificity of the derivatives towards target DNA [285]. The construction of fullerene–DNA hybrid materials allows transmission electron microscopy (TEM) imaging of deoxyribonucleic acid without the use of any heavy metal. Recently, such compounds became available and were shown to bind to DNA through electrostatic interactions with the phosphated groups, providing excellent contrast for imaging individual DNA molecules [281].
Oligo: 5'-TTT-TC'T-TTT-C'C'C'-C'C'-T-3'
C' = methylated cytosine
The major drawback in the development of fullerene compounds in medical chemistry is their poor solubility in water and particularly in physiological media. In principle, the introduction of polar side chains [286] or even the synthesis of positively charged fullerene derivatives [287] could circumvent this problem by giving enhanced polarity, solubility, and high affinity for biological membranes. To this end, several fulleropyrrolidine materials were synthesized utilizing the methodology of 1,3-dipolar cycloaddition of azomethine ylides to C$_{60}$. These novel derivatives were found to be soluble in water at sufficiently high concentrations (10$^{-4}$–10$^{-5}$ M l$^{-1}$) to allow biological assays [288]. However, the most water-soluble organofullerene material, up to now, was synthesized via the cyclopropagation route; its structure is based on a dendrimer moiety while the high solubility in water has been attributed to the 18 carboxylic groups located in the periphery of the fullerodendrimer [289]. Also, some unnatural amino acids have been synthesized containing fullerenes. The first example concerns fullero-proline in which a proline ring is fused to a 6,6 junction of C$_{60}$ [290]. Fullero-proline was conceived as a building block for the construction of fullerene-based peptides [291]; however, the designed synthetic route resulted in the isolation of its racemic mixture, while enantiomeric resolution relied on chiral chromatography [292]. Lately, the synthesis of a protected fullerene-functionalized amino acid and its use in solid-phase synthesis for the preparation of a water-soluble peptide was achieved (Scheme 16) [293, 294].

In other recent reports concerning enzymatic inhibition and receptor binding of organofullerene materials, C$_{60}$ monomalonate adducts were found to selectively inactivate the neuronal nitric oxide synthase isoform in a manner completely preventable by the concurrent presence of superoxide dismutase and catalase [295]. Also two fullerene–steroid hybrids were synthesized and found to decrease both the ATP hydrolysis and Ca$^{2+}$ uptake activity of SR Ca$^{2+}$-ATPase while the inhibitions were concentration dependent [296].

8.2 Endohedral Metallofullerenes

As the leading commercially available contrast-enhancing agents for magnetic resonance imaging (MRI) are gadolinium(3+) chelates [297], endohedral metallofullerenes encapsulating gadolinium ions could provide improved materials for such purposes. In fact, the unique electronic structure of gadolinium that contains seven unpaired electrons is combined with the advantage of locking up this heavy and otherwise toxic metal inside the carbon cage away from important biomolecules and tissues. In addition, fullerenes offer the possibility of accommodating more than one gadolinium atom inside their hollow space providing extra activity. However, in order to test these materials in vivo, they must be made soluble in highly polar solvents and water, to be inserted into tissues and to dissolve in aqueous fluids. This obstacle was eliminated by functionalization of endohedral metallofullerene materials with the proper organic groups that eventually give the desired solubility. The easiest way to do so was by multihydroxylation of the outer sphere of the cage. In fact, the polyhydroxylated gadolinium endohedral metallofullerene Gd@C$_{82}$(OH)$_x$ was synthesized and found to possess
almost 20 times better signal enhancement as an MRI agent in comparison to the commercially available ones, even at much lower gadolinium concentrations [298–300]. In addition, by a modification of the Bingel cyclopropanation reaction, a product containing ten malonate groups was prepared, providing Gd@C_{60} [C(COONa)_{2}]_{10} [301]. The synthesized material was found to be as effective as the commercially available gadolinium chelate MRI agents. Finally, a new functionalized gadolinium endohedral metallofullerene was announced. Utilizing the same type of reaction for the modification of Sc_{3}N@C_{80}, namely Diels–Alder [4+2] cycloaddition of 6,7-dimethoxyisochroman-3-one, the corresponding trimetallic nitride endohedral metallofullerene derivative, Gd_{2}ScN@C_{80} was synthesized with the perspective to be water soluble once the methoxy groups of the isochromanone moiety are replaced with carboxylic ones [302].

Another promising application of endohedral metallofullerenes lies in the field of nuclear medicine. Endohedral metallofullerenes could potentially provide a unique alternative to chelating compounds because of their resistance to metabolism and their high kinetic stability. The major disadvantage of the current radiopharmaceutical drugs that contain chelated radioisotopes of metals for imaging is their in vivo kinetic instability, which can allow the release of small quantities of toxic radiometals. Once the toxic heavy radioactive metal is placed inside the fullerene cage, it will have no chance to escape. Biodistribution studies of radioactive $^{166}$Ho@C_{82}(OH)_{x} in mice have been performed and the theory that endohedral metallofullerenes can act as radiotracers for in vivo studies was verified [295, 303]. Among the most important findings is that endohedral metallofullerol $^{166}$Ho@C_{82}(OH)_{x} has a blood pool residency time of over an hour with nearly total clearance from blood shortly thereafter, and was not acutely toxic in vivo at the doses tested.

9 Quantum Computing

Tremendous progress has been made in the fundamental theory of quantum information and there is currently a global race to find a practical technology for quantum computing. Quantum computation is potentially the most innovative area that can be addressed within nanotechnology, embracing nanofabrication and molecular nanotechnology, as well as atomic and molecular manipulation and assembly.

Research on modeling of endohedral fullerenes within single-walled carbon nanotubes (SWNTs) has received increased attention towards the understanding of their electronic and structural properties [304–307]. However, very recently particular emphasis was given to the endohedral fullerenes N@C_{60} [308–313] and P@C_{60} [314] due to the electron spin on the nitrogen or phosphorus site, respectively. Having an extremely long decoherence time the unpaired electron spin could be used as a qubit within a quantum computer.

Although atomic nitrogen and phosphorus are usually very reactive species, upon encapsulation they do not react with C_{60} while their electrons possess a long-lived spin. That spin can play the role of a natural quantum information unit with its two states “up” and “down” similar to the classical “1” and “0” states. Going one step further, because of the shielding by C_{60} the qubit in the fullerene
can form superposition states with long coherence times. According to this, electron-spin qubits could communicate with one another via the electronic states of the nanotube material.

Currently, dimers of $C_{60}$ with one filled moiety such as $N@(C_{60})_2$, have been synthesized and found to be stable enough [315]. Thus, in such a way, molecular arrangements of well-isolated spins using this type of endohedral fullerene can be suitably designed. Doubly filled dimer molecules and longer all-endohedral fullerene chains are obtainable using pure endohedral starting material. In such chains, all endohedral fullerenes will be of the same type. There exists, however, a possibility to create chains of ordered sequences of differently filled fullerenes by using the key-lock principle. A possible route is depicted in Scheme 17.

This example shows a minichain $N@C_{60}XY-P@C_{60}$, where X and Y are specially designed molecular bridging groups (the individual adducts $N@C_{60}$-X and $P@C_{60}$-Y should be synthesized first and in the following step they should be connected together, e.g., $X=R-NH_2$, $Y=R'-COOH$) [316]. In this approach, no local control of qubit–qubit interaction strength is needed. However, as this kind of research is still in its infancy various factors should be taken into account, like the flexibility or rigidity of the bridging molecules X and Y. Furthermore, with the advantage of the high solubility these organofullerene materials possess there are great possibilities to embed and align them in liquid crystals. Thus, the realization of an electron-spin quantum computer with a small number of qubits is feasible with this concept. Hundreds of operations should be possible using endohedral dimer molecules oriented in a liquid crystal as an elementary building block. More sophisticated molecular arrangements can be built using state-of-the-art fullerene chemistry.

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References

Electronic Structure and Energetics of Fullerites, Fullerides, and Fullerene Polymers

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Abstract
Cohesive mechanisms and electronic properties of C60 fullerites, various C60 compounds including superconducting alkali fullerides and alkaline-earth fullerides, and polymerized C60 materials studied in the framework of the density functional theory are reported. In various environments C60 shows different cohesive mechanisms, i.e., van der Waals cohesion, ionic cohesion, metallic cohesion, and even covalent bonding. C60 is an atomlike building block of new materials but has rich properties which one single atom can never show. The presence of two different facets on C60, pentagons and hexagons, is pointed out to be very important in considering their solid-state electronic properties.

Keywords
C60 · Fullerene · Fullerite · Fulleride · C60 polymer · Superconductivity · Density functional theory

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1 Introduction

In the last two decades, atomic clusters have attracted great interest first in physics and chemistry, and later in materials science and engineering. Most of the elements in the periodic table have been confirmed to possess their cluster phases, where the geometrical arrangement of atoms is entirely different from that of the bulk infinite phase. Accordingly, their physical and chemical properties are often distinct from those of the bulk phase [1].

In the case of metal clusters, for example, valence electrons show the shell structure which is characteristic of the system consisting of a finite number of fermions confined in a spherical potential well [2]. This electronic shell structure, in turn, motivated some theorists to study clusters as atomlike building blocks of materials [3]. The electronic structure of the metallofullerenes La@C_{60} [4] and K@C_{60} [5] was investigated from this viewpoint. This theorists’ dream of using clusters as atomlike building blocks was first realized by the macroscopic production of C_{60} and simultaneous discovery of crystalline solid C_{60}, where C_{60} fullerenes form a close-packed crystalline lattice [6].

Ever since this breakthrough, C_{60} has been intensively studied and has shown its rich “bonding” characteristics in various environments, from van der Waals cohesion to ionic and metallic cohesions, and even to the extent of covalent bonding, together also with its rich electronic properties including high transition-temperature (T_c) superconductivity in alkali-doped C_{60} fullerides. This article reviews the first-principles quantum-mechanical studies of these electronic and bonding properties of C_{60}.

2 Density Functional Theory Applied to Carbon

The density functional theory (DFT) [7, 8] is now widely used in studying both infinite bulk crystalline materials and finite atoms, molecules, and clusters. In principle, the ground-state total energy as well as the electron density itself in interacting many-electron systems is accurately described in DFT. Therefore, the geometry optimization by minimizing the total energy should also be accurate in DFT as well. The electronic band structure is, on the other hand, a very useful but approximate physical concept based on the quasiparticle theory for inter-
acting electrons. As far as the quasiparticle picture holds, DFT eigenstates are known to describe well the quasiparticle states.

If a one-body approximation such as the Hartree–Fock approximation gives a good picture, the quasiparticle state coincides with the Bloch state of the one-body approximation. However, the quasiparticle concept holds beyond the regime of one-body approximations, and the band structure of real materials should be considered not as a dispersion relation of one-body-approximation states but as that of quasiparticle states. In the case of silicon, for example, band theory has played a crucial role in its technological applications in last 50 years. The Hartree–Fock band structure finally obtained in the 1980s was found to deviate significantly from the band structure which was obtained using experimental values and had been used so far. The valence-band width, for example, is wider by as much as 5 eV than the experimental value. The local-density approximation (LDA) in the framework of the DFT gives a width of 12 eV, which agrees very well with experiment [9].

As for the fundamental gap of semiconductors, the LDA is known to underestimate its width, typically from half to two thirds of experimental values, while the Hartree–Fock gap is again much worse, for example more than five times larger than the experimental value in the case of silicon. In the case of covalent-bond materials including carbon, the LDA band structure is in general expected to be accurate, while the fundamental gap value should be considered to be larger in semiconductors than the LDA value.

In most LDA studies reported in this article, the Ceperley–Alder exchange-correlation formula is used [10, 11]. Also the norm-conserving pseudopotentials of Troullier and Martins are used [12]. Therefore, one only has to deal with the valence electrons in solving the self-consistent Kohn–Sham equations in the LDA. As for basis functions, plane waves with the cutoff energy of 50 Ryd are used.

The present formalism applied to carbon materials is confirmed to give accurate geometries with a typical error of only 1%. The diamond bond length obtained

Fig. 1 Geometry of C60. There are two kinds of bonds, r1 and r2
in the LDA (experiment) is 1.525 Å (1.540 Å), and that of graphite is 1.402 Å (1.421 Å). Even the interlayer distance of graphite can be well reproduced in the LDA, although the gradient correction usually supposed to give better results than the LDA is known to fail for this. The lattice constant obtained in the LDA for “AB stacking” graphite is 3.273 Å, being close enough to 3.328 Å [13].

In the case of isolated $I_h$-symmetry C$_{60}$, there are only two kinds of bonds ($r_1$ and $r_2$ in Fig. 1). There are 60 longer bonds ($r_1$) and 30 shorter bonds ($r_2$). The latter bond is known to be more reactive, as will be seen later in polymerized C$_{60}$ materials. The LDA bond lengths for $r_1$ and $r_2$ are 1.433 and 1.378 Å, respectively [13]. They are again close to the experimental values of 1.458 and 1.401 Å [14]. Especially their difference ($r_1-r_2$) in the LDA, 0.055 Å, is very close to the experimental value of 0.057 Å.

3 Fullerites

An isolated $I_h$ C$_{60}$ cluster has the closed-shell electronic structure with the five-fold degenerate $h_g$ state as the highest occupied state and the three-fold degenerate $t_{1u}$ state as the lowest unoccupied state. Accordingly, solid C$_{60}$ has a semiconducting electronic structure with valence and conduction bands consisting of $h_g$ and $t_{1u}$ states of the C$_{60}$ cluster, respectively (Fig. 2) [15].

This correspondence of solid-state energy bands with the cluster states indicates that C$_{60}$ is not only geometrically but also electronically an atomlike building block of materials. In solid C$_{60}$, cluster states form Bloch states like atomic states in ordinary solids without such geometrical hierarchy.

Due to the closed-shell electronic structure of C$_{60}$, the cohesive mechanism of pristine solid C$_{60}$ is considered to be via van-der-Waals-type relatively weak in-

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**Fig. 2** a LDA electronic energy levels of C$_{60}$ (left panel) and the band structure of the fcc C$_{60}$ crystal (right panel). In the band structure panel, energy is measured from the valence band top at the X point. The optically allowed transitions with excitation energies less than 6 eV in an isolated C$_{60}$ are indicated by arrows. b Band structure of the fcc C$_{60}$ around the fundamental energy gap [15]
Fig. 3  LDA total energy of the fcc C\textsubscript{60} as a function of the lattice constant. The internal-geometry optimization gives rise to a further energy gain at short lattice constant region [16].

In Fig. 3, the LDA total energy of the face-centered-cubic (fcc) C\textsubscript{60} is shown as a function of the lattice constant [16]. At each lattice point C\textsubscript{60} is placed with the same highest-symmetry (T\textsubscript{d}) orientation. The equilibrium lattice constant obtained is about 14 Å, in reasonable agreement with the experimental value of 14.198 Å [17] which is known to vary as a function of the temperature and orientational arrangements of C\textsubscript{60}. At room temperature, it is known that each C\textsubscript{60} cluster at the fcc lattice point rotates freely. At lower temperature, on the other hand, they form an orientationally ordered phase with four C\textsubscript{60} clusters per orientational simple-cubic (sc) unit cell [18, 19].

Although the overall semiconducting nature remains unchanged upon orientational ordering, the details of the band dispersion show an interesting change. In Fig. 4, the band structure of the orientationally ordered sc solid C\textsubscript{60} and that

Fig. 4a, b  Energy bands of a orientationally ordered simple-cubic solid C\textsubscript{60} and b of the fcc solid C\textsubscript{60} shown in the same simple-cubic Brillouin zone. The generalized tight-binding method is used [20].
of the fcc solid C\textsubscript{60} are shown [20]. Both are along the symmetry line of the sc unit-cell Brillouin zone. There are 240 C atoms in the sc unit cell and therefore the generalized tight-binding (TB) method is used instead of the LDA. The TB method used is constructed so as to reproduce well the band structure of the fcc C\textsubscript{60} as well as that of graphite.

The most important change to be noted is the appearance of a new gap in the \( t_{1u} \) conduction band. The lower and upper subbands can accommodate four and two electrons per C\textsubscript{60}, respectively. As will be discussed in the next section, there are various fullerides with electrons doped into their conduction bands. The appearance of the new gap in the conduction band indicates therefore that there is a possibility for orientational ordering to induce a metal–insulator transition in electron-doped C\textsubscript{60} fullerides.

4 Fullerides

4.1 Overview

After the production of crystalline solid C\textsubscript{60}, various C\textsubscript{60} compounds with metallic elements called “fullerides” have been produced. In Fig. 5, alkali and alkaline-earth fullerides are summarized [21]. Since fcc (sc) C\textsubscript{60} has two tetrahedral (T) and one octahedral (O) interstitial sites per C\textsubscript{60}, there are various fcc \( A_3C_{60} \) fullerides, where \( A=Na, K, Rb, Cs \) or their combinations. Interestingly, most of them

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Fig. 5 Various C\textsubscript{60} fullerides with alkali and alkaline-earth metal atoms [21]
are superconductors with the highest transition temperature of 33 K in Cs₂RbC₆₀ [22, 23]. In most of these A₃C₆₀ superconductors, C₆₀ is known to take the highest-symmetry orientation as is chosen in the theoretical electronic-structure study of solid C₆₀. K or larger ions can be accommodated at the small T site only when C₆₀ takes the highest-symmetry orientation, which gives a hexagonal hole directed to the T site. There are still two equivalent highest-symmetry orientations for each C₆₀, and it is believed that C₆₀ randomly takes one of two orientations (“merohedral disorder”) [24].

Further doping of K or larger alkali atoms gives rise to a change of the C₆₀ lattice geometry from the close-packed fcc to a more open body-centered lattice. In body-centered tetragonal A₄C₆₀ with A=K/Rb, merohedral disorder is also reported to be the case [25]. However, unlike fcc A₃C₆₀, the merohedral disorder is necessary for the body-centered lattice to be tetragonal, since C₆₀ itself does not have a four-fold symmetry axis and orientationally ordered body-centered A₄C₆₀ should become orthorhombic, as in the actual case of Cs₄C₆₀ [26].

Further doping up to six atoms per C₆₀ gives rise to an even more open body-centered-cubic (bcc) structure, in which there are six equivalent distorted tetrahedral interstitial sites per C₆₀ [27].

On the other hand, Ba- and Sr-doped C₆₀ fullerides mostly show similar lattice geometries except for Ba₃C₆₀ and Sr₃C₆₀, which are found to take already an open body-centered-cubic-type lattice with an orientationally ordered sc unit cell [28]. (The body-center-site C₆₀ is rotated by 90° with respect to the cube-corner-site C₆₀.) Ba₄C₆₀ and Sr₄C₆₀ are body-centered orthorhombic (bco) fullerides [29] as in the case of Cs₄C₆₀, and both Ba₄C₆₀ and Sr₄C₆₀ are superconductors. The bcc Ba₆C₆₀ and Sr₆C₆₀ fullerides are both metallic, unlike semiconducting A₄C₆₀ bcc fullerides. Another interesting bcc fulleride is A₃Ba₃C₆₀ (A=K/Rb) [30], in which A and Ba are reported to occupy randomly the interstitial sites of the bcc C₆₀ lattice. Both K₃Ba₃C₆₀ and Rb₃Ba₃C₆₀ are known to be superconductors.

4.2
Fcc K₃C₆₀

The LDA electronic band structure of fcc K₃C₆₀ is shown in Fig. 6a together with that of fcc pristine C₆₀ having the same lattice constant [31]. It is interesting to know that dispersion of the states near the Fermi level (E_F), from h₁u to t₁g states, is almost the same in the two systems, indicating a rather simple charge transfer from the K 4s state to C₆₀ conduction bands. Since the t₁u state can accommodate up to six electrons, it is just half occupied in K₃C₆₀, and the electronic structure becomes metallic. Therefore, the cohesion mechanism of K₃C₆₀ is considered to be primarily ionic with additional metallic cohesion.

4.3
Bcc K₆C₆₀

The simple charge transfer from K to C₆₀ observed in the fcc K₃C₆₀ is not always the case in potassium fullerides. Similar comparison between the LDA band structure of the bcc K₆C₆₀ fulleride and that of the hypothetical bcc pristine solid
C₆₀ is shown in Fig. 6b. It is evident that the fully occupied \( t_{1u} \) band, a new valence band of semiconducting K₆C₆₀, is considerably wider than that of the empty \( t_{1u} \) band of the pristine bcc C₆₀. This band widening upon introduction of K atoms takes place also for the \( t_{1g} \) conduction band. Such band widening is considered to be due to the presence of hybridization between the C₆₀ and K electronic states [32]. Therefore, the cohesive mechanism in semiconducting bcc A₆C₆₀ is primarily ionic with additional cohesion through the electronic hybridization.

Such interesting differences between fcc and bcc fullerides can be understood from the viewpoint of the C₆₀ geometry. Although all 60 atomic sites are equivalent in the \( I_h \) C₆₀, profiles of the electronic states above pentagons are different from those of hexagons. For example, the lowest unoccupied \( t_{1u} \) state is known to have more spatial distribution above pentagons than hexagons. There are 12 pentagons on the C₆₀ surface and each in the fcc lattice contacts its 12 neighboring fullerenes through those 12 pentagons. On the other hand, C₆₀ in the bcc lattice contacts its neighbors through hexagons. Therefore, C₆₀ \( t_{1u} \) states can have more overlap with each other in the fcc lattice to form wider conduction bands than in the bcc lattice. K doping into the interstitial sites in the fcc lattice has little effect on the conduction-band electronic states, since neither T nor O sites are surrounded by pentagons. In contrast, the interstitial site of the bcc C₆₀ lattice is surrounded by two pentagons as well as two hexagons, and K doping can give rise to a sizable hybridization between the C₆₀ \( t_{1u} \) and K 4s states.

4.4 K₃Ba₃C₆₀ and Rb₃Ba₃C₆₀

In the case of fcc A₃C₆₀ superconductors, the \( t_{1u} \) conduction-band width depends strongly on the C₆₀-C₆₀ distance which is mostly determined by the ionic radii of interstitial-site alkali atoms. The larger ion gives rise to a longer interfullerene distance, smaller overlap between neighboring \( t_{1u} \) states, narrower \( t_{1u} \) band width, and a larger density of states at the Fermi level, \( N(E_F) \). This is not the theory
which explained the variation of observed $T_c$ in $A_3C_{60}$ superconductors, but the theory which led to the discovery of new higher-$T_c$ materials [23].

In the case of $A_3Ba_3C_{60}$ superconductors, on the other hand, $T_c$ is higher for smaller $A$: 5.6 and 2.0 K for $K_3Ba_3C_{60}$ and $Rb_3Ba_3C_{60}$, respectively. This difference between fcc and bcc superconductors may be due to the hybridization of alkali and $C_{60}$ states in the bcc fullerides mentioned above. Actually, the LDA electronic structure (Fig. 7) shows slightly larger $N(E_F)$ for $K_3Ba_3C_{60}$ than for $Rb_3Ba_3C_{60}$ [31].

The presence of hybridization between $K$ and $C_{60}$ states can be seen directly in the electron density obtained by the LDA. In Fig. 8, the valence electron densities of $K_3Ba_3C_{60}$ and those of the hypothetical bcc solid with the same $C_{60}$ geometry are shown together with their difference. A sizable electron density is found around K sites, although a larger density remains around Ba sites. The difference density clearly shows that charge transfer from not only Ba but also from the K atom is incomplete [32].

**Fig. 7** Energy bands of superconducting $K_3Ba_3C_{60}$ and $Rb_3Ba_3C_{60}$ fullerides, together with their electronic density of states. Although the lattice constant is definitely longer in $Rb_3Ba_3C_{60}$ than in $K_3Ba_3C_{60}$, the band dispersion shows very little difference in the two materials, and the Fermi-level density of states is slightly higher in $K_3Ba_3C_{60}$ than in $Rb_3Ba_3C_{60}$ [31].

**Fig. 8** a Valence electron density of the (100) plane of $K_3Ba_3C_{60}$, b that of the pristine bcc solid $C_{60}$, and c the difference between them. In c, positive-value regions are shown. The center of $C_{60}$ is located at each corner. Each contour line indicates twice (half) the density of the neighboring thinner (thicker) contour lines [32].
It is evident from Fig. 8 that Ba states show stronger hybridization with C\textsubscript{60} states than K states. It has been pointed out that the Ba 5\textit{d} state should play an important role in Ba fullerides [33].

The 5\textit{d} state of a neutral Ba atom is energetically higher than the 6\textit{s} state and therefore empty. On the other hand, in the Ba\textsuperscript{2+} ion, the 5\textit{d} state becomes lower than the 6\textit{s} state. This interchange of the energy sequence of these states means that the 5\textit{d} state tends to accept electrons which are originally going out from the Ba 6\textit{s} state to counter ions in the compound phase. Therefore, the charge transfer from Ba should be incomplete in Ba fullerides. In other words, Ba 5\textit{d} and C\textsubscript{60} states hybridize rather strongly.

This hybridization should also take place in the bco Ba\textsubscript{4}C\textsubscript{60} superconductor. Figure 9 shows its electronic band structure [34]. The importance of the hybridization is evident. Splitting of the three \textit{t}\textsubscript{1g} states at the gamma point is found to be as large as 0.9 eV. This splitting is originally induced due to the lower symmetry of the orthorhombic lattice. However, the splitting in the hypothetical pristine bco C\textsubscript{60} with the same lattice geometry is less than half. Therefore, the hybridization in Ba\textsubscript{4}C\textsubscript{60} plays a very important role in determining the conduction-band width.

5 Fullerene Polymers

Discovery of crystalline solid C\textsubscript{60} was actually the finding of a new form of crystalline carbon, being different in dimensionality from graphite, two-dimensional \textit{sp}\textsuperscript{2} carbon. It is also different from diamond, three-dimensional \textit{sp}\textsuperscript{3} carbon. From this viewpoint, crystalline C\textsubscript{60} polymers produced via high-pressure and
high-temperature treatment of the pristine C\textsubscript{60} are actually to be classified as another new form of carbon [35, 36]. They consist both of \textit{sp\textsuperscript{2}} and \textit{sp\textsuperscript{3}} carbon atoms, and possess several distinct phases: a one-dimensional orthorhombic phase, a two-dimensional “tetragonal” phase, and a two-dimensional rhombohedral phase.

In these three polymerized pristine C\textsubscript{60} materials, a four-membered ring always appears at the interfullerene bonding area. Originally shorter “double” bonds (\textit{r\textsubscript{2}}-bonds in Fig. 1) on neighboring fullerenes open up to form a pair of interfullerene bonds, forming a four-membered ring.

The valence electron density of the tetragonal-phase polymer is shown in Fig. 10a [37]. It is evident from the figures that this tetragonal phase should have different in-plane lattice constants (\(a\) and \(b\)) if the stacking is a simple “AA” type with a body-centered lattice. It has been reported recently that it is actually the case in this polymer, and the material has a pseudo-tetragonal orthorhombic lattice [38].

The electronic structure of this tetragonal phase is semiconducting (Fig. 10b). Interestingly, the LDA fundamental gap value is 0.72 eV, being smaller than that of the fcc C\textsubscript{60}. Introducing \textit{sp\textsuperscript{3}} carbon into the originally \textit{sp\textsuperscript{2}} carbon lattice does

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\textbf{Fig. 10}  \textbf{a} Contour map of the valence electron densities of the “tetragonal” C\textsubscript{60} polymer on the (001) plane (\textit{left panel}) and (010) plane (\textit{right panel}). The difference between each neighbor contour is 0.021 atomic units. The projected C–C network on the (001) plane is also shown. \textbf{b} Its electronic energy band. The material is a semiconductor with a smaller band gap than the pristine fcc C\textsubscript{60} [37]
reduce the fundamental gap here. Although the pure $sp^3$ carbon, diamond, possesses a much larger fundamental gap to be a good insulator, its gap is between the bonding and antibonding $\sigma$ states, while the gap in the $sp^2$--$sp^3$ C$_{60}$ polymer here is between the bonding and antibonding $\pi$ states. Therefore, it is not surprising for polymerized C$_{60}$ materials to have a smaller gap than that of the all-$sp^2$ pristine solid C$_{60}$.

Another two-dimensional C$_{60}$ polymer phase is the rhombohedral phase, in which the (111) plane of the original fcc C$_{60}$ lattice is the polymerized plane (Fig. 11). If the unit in the rhombohedral cell is spherical or, at least, has a six-fold symmetry along the axis perpendicular to the plane, the stacking sequence is unique. However, each polymerized C$_{60}$ unit only has a three-fold symmetry along the axis, and there can be two different ways of stacking, “ABC” and “ACB”, where B and C correspond to the polymerized plane with the C$_{60}$ positions above the B and C sites in Fig. 11, respectively [39].

Originally the ACB stacking was proposed, while a recent single-crystalline X-ray refinement clarified that this rhombohedral polymer takes the ABC stacking [40]. The LDA total energy for the ABC stacking is actually found to be slightly lower than that of the ACB stacking, while their difference is rather marginal, about 0.01 eV per C$_{60}$. The total energy itself is found to be lower than that of an isolated C$_{60}$ cluster by about 0.5 eV, but is slightly (about 0.2 eV) higher than that of the fcc C$_{60}$ [39].

The LDA electronic band structure of the ACB-stacking rhombohedral polymer was reported to be semiconducting with an indirect fundamental gap.

![Fig. 11](image_url) Polymerized plane of the rhombohedral C$_{60}$ polymer phase. On the top (bottom) of each C$_{60}$ there is a hexagon, which is surrounded by three pentagons (indicated by shaded circles) and three hexagons. The next plane should have C$_{60}$ units either on “B” or “C”, giving rise to the “ABC” and “ACB” stackings, respectively [39]
LDA study on the ABC stacking confirmed that the material is a semiconductor. The band dispersion in the valence-band region is found not to depend strongly on the stacking sequence, while the lower conduction-band region shows a little stacking dependence (Fig. 12). The fundamental gap value is found to be larger in the actual ABC stacking case than the ACB stacking case by about 0.1 eV. A larger gap in the ABC stacking is consistent again with the C\textsubscript{60}−C\textsubscript{60} contact geometries. In the ACB stacking, each C\textsubscript{60} has a contact with next-layer C\textsubscript{60} through pentagons, while in the ABC stacking contact is through hexagons. The $t_{1u}$ conduction-band states should show, therefore, stronger dispersion in the ACB stacking to give a wider conduction band and narrower fundamental gap [39].

These electronic properties of the rhombohedral-phase polymer are, for the optimized internal geometry, within the LDA under experimentally observed lattice constants. Bond lengths around the interfullerene-bonding area in the

**Fig. 12a, b** Electronic band structure of the rhombohedral C\textsubscript{60} polymer with a ACB stacking and b ABC stacking, respectively. In each case, the electronic density of states is shown (in arbitrary units); energy is measured from the valence band top. The two systems show very similar valence-band dispersions, while the conduction-band states show a little difference in their dispersion. The fundamental gap of the ABC stacking polymer (lower panels) is found to be narrower than that of the ACB stacking polymer (upper panels) [39]
Fig. 13  Bond lengths of the rhombohedral C$_{60}$ polymer around the interfullerene bonds (Å). Experimentally proposed values are also shown in parenthesis [39]. Both values generally show good agreement with each other.

geometry are shown together with the values proposed from the X-ray diffraction analysis (Fig. 13) [39]. They show good agreement with each other [39, 40].

The LDA electronic structure for the one-dimensional orthorhombic polymer phase shows that it is also a semiconductor, while a rather strong chain-orientation dependence is also found. The LDA fundamental gap value also depends on the chain orientation, while the value itself is larger than that of two-dimensional polymers [41].

Although the possibility of three-dimensional C$_{60}$ polymer has been discussed experimentally, so far the polymerized crystalline solid C$_{60}$ phases with firm experimental evidence reported are in the above three phases. On the other hand, theoretically the three-dimensional C$_{60}$ polymer phase has been proposed from the LDA total-energy optimization under the reduced lattice constants (Fig. 14) [42]. The tetragonal phase is found to go to the three-dimensionally polymerized phase with as many as 24 \( sp^3 \) carbon atoms at about 20 GPa pressure. Interestingly, this three-dimensional polymer phase is predicted to be metallic with large \( N(E_F) \).

6 Concluding Remarks

As has been discussed in this article, C$_{60}$ fullerene has shown its rich cohesive properties in various environments. It can form a van der Waals solid in the pristine phase and in other compound materials with various molecules. In fullerides, i.e., the compounds with metallic elements, valence electrons of metal atoms transfer to C$_{60}$ partly or almost completely, depending on the lattice geometries and electronic properties of the metallic elements. So fullerides are ionic solids. Interestingly, these ionic fullerides often possess metallic electronic structure and show superconductivity. The importance of the superconductivity of C$_{60}$ fullerides is not only in its relatively high \( T_c \) values but also in its wide
Fig. 14  

(a) LDA total energy of the “tetragonal” C$_{60}$ polymer under uniaxial stress. At shorter interlayer distances, a new phase is found to appear. The inset panels show radial distribution functions for the original two-dimensionally polymerized material and that of the new stable phase. 

(b) Geometry of the new stable phase, which turns out to be three-dimensional polymer with 24 $sp^3$ C atoms and 36 $sp^2$ C atoms per C$_{60}$ [42]
variety of materials, with wide range of $T_c$ values. A further surprise of C$_{60}$ in its cohesive properties was its ability to condense, via covalent bonding, with several different numbers of interunit bonds.

These rich bonding and cohesive properties of C$_{60}$ revealed after its macroscopic production are far beyond the expectation of theorists who dreamed of using clusters as atomlike building blocks of new materials. In the era of nanoscience and nanotechnology, C$_{60}$ and other fullerenes will continue to play an important role.

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7 References

Charge Density Level Structures of Endohedral Metallofullerenes by the MEM/Rietveld Method

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Abstract The bonding nature of metal atoms encapsulated in fullerene cages is important structural information relating to the stability of the metallofullerene endohedral structure. Experimental charge density studies of endohedral metallofullerenes by synchrotron radiation (SR) powder diffraction utilizing the maximum entropy method (MEM) are reviewed. Results of the endohedral metallofullerenes La@C₈₂, Sc@C₈₂, Sc₂@C₆₄, La₂@C₈₀, Sc₀@C₈₂, Sc₂@C₆₆, and Sc₂C₂@C₈₄ are given. The precise MEM charge densities of the metallofullerenes reveal the existence of ionic and/or covalent bonding between metal atoms and the carbon cage, as well as the feature of thermal motion of metal atoms inside the carbon cage. The MEM/Rietveld method, which is the crucial method for data analysis in order to determine the endohedral structure of the fulleride, is also mentioned in some detail.

Keywords Metallofullerene · Synchrotron radiation · Maximum entropy method · Charge density · Powder diffraction

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Abbreviations

MEM  Maximum entropy method
SR    Synchrotron radiation

1 Introduction

Endohedral metallofullerenes, which encapsulate metal atoms in a carbon cage, are now becoming one of the attractive key materials for nanotechnology. Since the determination of the endohedral structure of \( \text{Y}@\text{C}_{82} \) in 1995 [1], various endohedral structures of metallofullerenes have been revealed by X-ray structure analysis by our group [2–9]. The obtained results improved understanding of the stability of the metallofullerene endohedral structure and stimulated creation of novel endofullerene-related materials.

The difficulties of X-ray structure analysis of fullerene compounds come from the fact that the intrinsic orientational disorder of the fullerene cage is rather common, like other molecular compounds. In such a case, it may be extremely difficult to construct an adequate structural model. For the structural analysis we used a new elaborated method, the maximum entropy method (MEM) [10–13], which is different from the conventional Fourier method. The MEM is basically a statistical deduction method based on theoretical information of entropy. The MEM can yield a high-resolution density distribution from a limited number of diffraction data. The obtained density distribution yields detailed structural information without using a structural model. The ability of the MEM in terms of a model-free reconstruction of the charge densities from measured X-ray diffraction data can be interpreted as “imaging of diffraction data” [11]. The method is further developed by combining with the Rietveld method [14], that is, the MEM/Rietveld method [1, 9]. The method is very powerful for creating structural images at the charge density level when it is applied to synchrotron radiation (SR) powder diffraction data. The obtained MEM charge densities provide not only information on the atomic positions but also on the bonding nature of the encapsulated metal atom. The purpose of this review is to illustrate the power of the MEM/Rietveld method for the charge density level structure analysis of metallofullerenes utilizing SR powder diffraction data and to present a variety of endohedral structures.

2 Synchrotron Radiation Powder Experiment

All of the structures of the metallofullerenes described in this review were determined by SR powder data. Third-generation SR has many of the advantages of X-ray structural studies of powder specimens. Firstly, intense incident X-ray photons make it possible to collect a whole powder pattern rapidly. Secondly, it is also possible to collect high angular resolution data utilizing the high parallel beam of SR. The large Debye–Scherrer camera installed at SPring-8, BL02B2, is designed
to be suitable for materials scientists’ needs rather than to be the highest-resolution powder instrument in the world [15]. The imaging plate (IP) is employed as detector to collect a whole powder pattern simultaneously. This should contribute not only to a rapid collection of data but also to the reliability of the collected data, because it can guarantee that the whole powder pattern is collected under the same experimental conditions. Though the pixel size of the IP can be chosen as 50×50 or 100×100 μm, the former is normally used to get enough data points for powder profile expression. The radius of the camera is 286.5 mm, which corresponds to 0.01° in 2θ in the case of 50×50-μm pixels. The size of the IP is 200×400 mm, which covers up to 80.0° in 2θ. As the maximum diffraction angle, 80.0° may not sound large enough. But taking into account utilization of short-wavelength incident X-rays, e.g., 0.5–1.0 Å, it can cover a much wider reciprocal space (d>0.4–0.8 Å) than the CuKα case. The actual camera is shown in Fig. 1 with a schematic drawing.

The sample preparation of endohedral metallofullerenes was done by Shinohara and details are described in the review article [16]. The soot containing M@C_{2n}(M=Sc and La) was produced in direct-current (300–400 A) spark mode under He flow at 50 torr and collected under totally anaerobic conditions. The target fullerenes were separated and isolated from the various hollow fullerenes (C_{60}–C_{110}) and other metallofullerenes by the two-stage high-performance liquid chromatography (HPLC) method by using two complementary types of HPLC columns. The purity of the metallofullerenes used for structure analysis relative to other fullerenes was always more than 99.9%.

The powder sample grown from toluene solvent was sealed in a silica-glass capillary (0.3 mm inside diam.). The amounts of metallofullerene sample were quite small and less than 10 mg. All of the results presented in this article were obtained at room temperature. For the precise MEM charge density study, data measurement with more than 2,000,000 counts as maximum intensity was carried out with the longer exposure time of, e.g., 50–100 min, which gives the best possible counting statistics with the large Debye–Scherrer camera at BL02B2.

![Fig. 1](image_url)  
**Fig. 1**  a Photograph and b schematic drawing of the large Debye–Scherrer camera at SPring-8 BL02B2
3
The MEM/Rietveld Method

In 1995, an elaborated method was developed for accurate structure analysis using X-ray powder diffraction data, that is, the MEM/Rietveld method [1, 9]. The method enables us to construct the fine structural model up to charge density level, and is a self-consistent analysis with MEM charge density reconstruction of powder diffraction data. It also includes the Rietveld powder pattern fitting based on the model derived from the MEM charge density. To start the methods, it is necessary to have a primitive (or preliminary) structural model. The Rietveld method using this primitive structural model is called the pre-Rietveld analysis. It is well known that the MEM can provide useful information purely from observed structure factor data beyond a presumed crystal structure model used in the pre-Rietveld analysis. The flow chart of the method is shown in Fig. 2.

3.1
The MEM/Rietveld Analysis of La@C\(_{82}\)

As an example, the process of the MEM/Rietveld analysis is presented for monometallofullerene, La@C\(_{82}\) [2]. The sample of La@C\(_{82}\) crystal included solvent

![Flow chart of the MEM/Rietveld method](image.png)
Fig. 3 The process of estimation of observed intensities in MEM/Rietveld analysis.
toluene molecules. The space group of the crystal was assigned to be P2\(_1\), which is monoclinic \([a=18.3345(8)\ \text{Å}, \ b=11.2446(3)\ \text{Å}, \ c=11.2319(3)\ \text{Å}, \ \text{and} \ \beta=107.970(6)^\circ]\).

This method requires only a crude structural model as a starting model. In this analysis, the starting model was a homogeneous spherical shell density for the carbon cage. As for the temperature factors of all atoms, an isotropic harmonic model was used: an isotropic Gaussian distribution is presumed for a La atom in the starting model. Then, the radius of the \(C_{82}\) sphere was refined as structural parameter in the Rietveld refinement.

The process of observed intensity estimation for overlapping reflections in the Rietveld analysis is shown schematically in Fig. 3. Suppose we have partially overlapped 1- and 2-reflections as shown in Fig. 3a. Observed structure factors were evaluated by dividing the observed intensities at each data point, \(Y_{\text{obs}}(\theta)\), into the \(Y_{\text{1obs}}(\theta)\) and the \(Y_{\text{2obs}}(\theta)\) based on the calculated contributions of individual reflections, \(Y_{\text{1cal}}(\theta)\) and \(Y_{\text{2cal}}(\theta)\). This evaluation is done by the following Eq. 1 in a modified Rietveld-refinement program as shown in Fig. 3b,

\[
Y_{\text{1obs}}(\theta) = Y_{\text{obs}}(\theta) \times \frac{Y_{\text{1cal}}(\theta)}{Y_{\text{1cal}}(\theta) + Y_{\text{2cal}}(\theta)}
\]

where \(Y_{\text{obs}}(\theta)\) and \(Y_{\text{cal}}(\theta)\) are the observed and calculated intensity at the diffraction angle \(\theta\).

The reliability factor (R-factor) based on the Bragg intensities, \(R_p\), and the weighted profile R-factor, \(R_{wp}\), were 11.6 and 2.1%, respectively. The result of the first Rietveld fitting is shown in Fig. 4a. In the figure, the Debye–Scherrer pattern recorded on the IP is inserted. Although the fitting of the observed data with the calculated powder pattern is not so good, the MEM charge density can be obtained with the observed structure factors derived in this analysis. The number of structure factors derived in this analysis was 279. Following this Rietveld analysis, a MEM analysis was carried out using 84×56×56 pixels by computer program, ENIGMA [17].

The MEM charge density based on pre-Rietveld analysis is shown in Fig. 5 and clearly exhibits a hemispherical feature corresponding to the encapsulated La atom together with the presence of \(C_{2v}\) cage symmetry. The structure model for the next Rietveld refinement was, thus, modified into such a hemispheric charge density of the La atom in the \(C_{2v}-C_{82}\) cage. The preliminary density model with a homogeneous spherical shell was modified so as to fit a theoretical \(C_{2v}\) cage structure according to an ab initio optimized geometry [18]. In the second Rietveld analysis, the positions of carbon atoms were optimized under the constraint of \(C_{2v}\) symmetry limited only to the \(C_{82}\) cage. The central position of the carbon-cage center and the \(C_2\) axis orientation were also optimized from the default values deduced from the first MEM map. In addition, the solvent toluene molecule was described as a CH\(_3\) part and a six-membered ring composed of five CH and one C components, to express the directional feature of a toluene molecule. As a result, the reliability factor (R-factor) based on the Bragg intensities, \(R_p\), and weighted profile R-factor, \(R_{wp}\), remarkably improved from 11.6 and 2.1% to 5.8 and 1.8%, respectively, in the Rietveld analysis. The final fitting result is shown in Fig. 4b.
\textbf{Fig. 4 a, b}  Fitting results of a the pre-Rietveld analysis and b the final Rietveld analysis for La@C_{82}.

\textbf{Fig. 5}  The (100) section of the MEM charge density of La@C_{82} based on pre-Rietveld analysis. Contour lines are drawn from 0.0 to 4.5 $e/\angstrom^3$ with 0.3 $e/\angstrom^3$ intervals.
3.2 The MEM Charge Density of La@C\textsubscript{82}

The (100) plane contour map of the final MEM charge density distribution is shown in Fig. 6. The contour lines are presented from 0.0 to 4.5 \textit{e}/Å\textsuperscript{3} with 0.3 \textit{e}/Å\textsuperscript{3} steps. The contours around the origin of the unit cell are due to the solvent toluene molecules. The C\textsubscript{82} cage is clearly seen in the figure. A hemispherical charge distribution, which should be due to the La atom, is recognized inside the cage. To confirm that the charge density of this hemispheric shape stems from the La atom encapsulated in the C\textsubscript{82} cage, the total charge of a three-dimensional hemispherical distribution is counted. The obtained result is 53.7 \textit{e}, which is close to the number of electrons of the triply charged state of the La ion (54.0 \textit{e}). It is concluded that the hemispheric feature represents the La atom distribution encapsulated inside the C\textsubscript{82} cage. It is also concluded that the electronic structure of La@C\textsubscript{82} can formally be expressed as La\textsuperscript{3+}@C\textsubscript{82}\textsuperscript{3–}.

The density maximum point in the La hemispheric density distribution, which corresponds to the most probable La atom position, locates adjacent to the center of a six-membered ring inside the C\textsubscript{82}/C\textsubscript{2V} cage. The nearest neighbor distance between the most probable La atom position and the carbon atom is 2.55(8) Å. The distance from the cage center to the La atom is 1.96(9) Å. This value is very close to those reported by theoretical calculations [19–21]. Furthermore, the obtained feature of the La atom density resembles a theoretically deduced electrostatic potential inside the C\textsubscript{82}\textsuperscript{3+}/C\textsubscript{2V} [21].

To visualize the three-dimensional shape of the fullerene cage and the La atom, an equi-charge density surface of La@C\textsubscript{82} is shown in Fig. 7. The equi-density level is 1.8 \textit{e}/Å\textsuperscript{3}. Figures 7a and b represent the side and the top views of the hemisphere, respectively. The characteristic hemispheric charge density of the La atom can be clearly seen along with the six- and five-membered rings inside the carbon cage. The potential for the La atom must be very shallow along the fullerene cage. The six- and five-membered rings on the C\textsubscript{82} surface can easily be seen. At this density level, the six-membered rings have holes at the center,
Fig. 7 a, b The equi-charge density surface of La@C₈₂ for a side view and b top view. The equi-density level is 1.8 e/Å³

whereas the five-membered rings are filled with electron clouds. To further clarify the six- and five-membered ring shapes, many equi-charge density surfaces are obtained by changing equi-contour level. At the equi-density surface of 2.0 e/Å³ (Fig. 8), holes are observed in the center of the five-membered rings. Based on these identifications of the six- and five-membered rings, it is concluded that the cage structure of La@C₈₂ has C₂ᵥ symmetry. A schematic representation of the C₈₂/C₂ᵥ cage is also shown in Fig. 8.

In the MEM/Rietveld analysis, each of the observed structure factors of intrinsically overlapped reflections (for instance, 333 and 511 in a cubic system) can be deduced by the structure model based on a free atom model in the Rietveld refinement. In such a case, the obtained MEM charge density will be partially affected by the free atom model used. In order to reduce such a bias, the observed structure factors should be refined based on the deduced structure factors from the obtained MEM charge density. The detail of the process is described in the review article [9, 22–24]. In addition, the phased values of structure factors based on the structure model used in Rietveld analysis are used in the MEM analysis. Thus, the phase refinement is also done for the noncentrosymmetric case as P₂₁ of Sc@C₈₂ crystal by the iteration of MEM analysis. The detail of the process is also described elsewhere [25]. All of the charge densities shown in this article are obtained through these procedures.

Fig. 8 The equi-charge density surface of La@C₈₂ and a schematic cage structure of C₈₂/C₂ᵥ. The equi-density level is 2.0 e/Å³
4
The La and Sc Atom Behaviors in the $C_{82}\text{Cage}$

By the MEM charge density studies, the different features of encapsulated metal atoms in $C_{82}$ were revealed for La@$C_{82}$ [2] and Sc@$C_{82}$ [3]. To compare the three-dimensional shape of the metal-atom charge distribution, a section of the equi-density surface of a La@$C_{82}$ molecule is presented in Fig. 9 together with the result for Sc@$C_{82}$ (Isomer I). The equi-density level is $1.8\ e/\text{Å}^3$. The number of electrons belonging to the Sc atom of Sc@$C_{82}$ was $18.8(2)\ e$, which is close to the $19.0\ e$ of a divalent state of the scandium atom, Sc$^{2+}$. This indicates that the Sc@$C_{82}$ (I) is an endohedral metallofullerene whose formal electronic structure is Sc$^{2+}C_{82}^2$. This result has brought the long discussion as to whether the Sc atom is in a divalent or trivalent state inside the carbon cage [26-29] to an end experimentally.

The characteristic hemispheric charge density of the La atom presents a contrast to the Sc feature in Sc@$C_{82}$. The potential for the La atom must be much shallower than for Sc along the fullerene cage. The six- and five-membered rings on the $C_{82}$ surface can easily be seen. Based on these identifications of the six- and five-membered rings, it is concluded that the cage structure of Sc@$C_{82}$ also has $C_{2V}$ symmetry.

It is quite unlikely that the unusual charge density distribution of La comes from a disordering of La atoms, because there are no local maxima in the bowl-like La charge distribution except for the peak maximum. If the observed feature of the La charge density is entirely due to a large thermal motion of the La atom inside the carbon cage, the La atom should vibrate $4-5\ \text{Å}$ along the cage. Such a dynamical (large amplitude) motion can be called a giant motion. An extremely shallow potential energy barrier for the La atom has to be responsible for such a giant motion, which has been predicted by a theoretical calculation [30]. The observed large-amplitude motion can primarily be understood by a somewhat larger La–cage distance than that obtained, for example, in La@$C_{82}$, which results in a weaker electrostatic interaction between the La atom and the $C_{82}$ cage [30].

![Fig. 9](image_url) Sections of the equi-density surface of the MEM charge densities for Sc@$C_{82}$ and La@$C_{82}$
The nearest La–C distance, 2.55(8) Å (ionic radius of La(III); 1.15 Å), is slightly larger than the nearest Sc–C distance, 2.53(8) Å (ionic radius of Sc(III); 0.81 Å), of Sc@C₈₂, which results in a weaker metal–cage interaction for La@C₈₂. In fact, the IR/Raman spectroscopic studies [31, 32] on metallofullerenes by metal–cage vibrational mode measurements indicated that the La–cage vibration is much smaller in energy than those observed in other M@C₈₂ (M=Y, Sc, Tm)-type metallofullerenes.

5 The Structure of Dimetallofullerene Sc₂@C₈₄

The dimetallofullerenes are interesting materials, because they might exhibit novel solid-state properties due to their very small band gaps [4, 33]. Ab initio theoretical studies [34, 35] and the experimental results on Sc₂@C₈₄ including scanning tunneling microscopy [36], transmission electron microscopy [37], and ¹³C-NMR [38] had suggested an endohedral nature. Consequently, we have determined the endohedral structure of the dimetallofullerene, Sc₂@C₈₄ (Isomer III). The result reveals that both Sc atoms are encapsulated within the carbon cage and that the Sc₂@C₈₄ (III) molecule has $D_{2d}$ symmetry.

The $R_I$-factor of the final Rietveld analysis was 7.9% (the weighted profile $R$-factor, $R_{wp}$=5.3%). The space group was assigned to $P2_1$, which is monoclinic. The cell parameters are determined as $a=18.312(1)$ Å, $b=11.2343(6)$ Å, $c=11.2455(5)$ Å, and $\beta=107.88(1)^\circ$. In Fig. 10a, the best fit of the Rietveld analysis of Sc₂@C₈₄ is shown. The MEM charge density analysis was carried out using 58×48×44 pixels. The reliability factor of the MEM charge density based on structure factors was 2.1% as shown in Fig. 10b. To visualize the three-dimensional configuration of the endohedral nature of the Sc₂@C₈₄, the MEM electron density distributions of Sc₂@C₈₄ are shown by an equi-contour surface of 1.3 e Å⁻³ in Fig. 11a. As a reference, a model structure of Sc₂@C₈₄ predicted by a theoretical study [28] is also shown in Fig. 11b. The cage structure clearly exhibits six- and five-membered rings. This configuration of the rings is exactly the same as that of the C₈₄/$D_{2d}$ cage. The two density maxima can be seen through the carbon cage. The number of electrons around each maximum inside the cage is 18.8(2) e, which is very close to that of a divalent scandium ion Sc²⁺ (19.0 e). Evidently, each of the two density maxima at the interior of the C₈₄ cage corresponds to a scandium atom, indicating that Sc₂C₈₄ is endohedral. A theoretical study has predicted that the formal electronic structure of Sc₂@C₈₄ is well represented by Sc²⁺₂@C₈₄⁺, where two 4s electrons of each Sc atom are transferring to the C₈₄ cage [34, 35].

In Fig. 12a, the higher equi-contour surface (2.5 e Å⁻³) of the MEM charge density is shown to see the Sc charge density feature. Two density maxima can be clearly seen through the carbon cage and are located symmetrically with respect to the center of the cage. The Sc–Sc distance in C₈₄ derived from the MEM charge density is 3.9(1) Å, which is a bit smaller than that of the theoretical value of 4.029 Å [34]. The nearest Sc–C distance is 2.4(2) Å (2.358 Å theoretical value [34]) (Fig. 12b). In Fig. 12a the charge density of the Sc atoms shows a salient teardrop feature as if the two Sc atoms (ions) are in a stretching vibration within the C₈₄ cage. The C–C distance of the double bond adjacent to the Sc atom is 1.9(3) Å.
**Fig. 10a, b** Fitting results a of the final Rietveld analysis and b based on the MEM charge density of Sc$_2$@C$_{84}$ shown in Fig. 11

**Fig. 11** a Equi-contour (1.3 e/Å$^3$) MEM density map of the Sc$_2$@C$_{84}$ molecule. b Schematic representation of the theoretically assumed structure model of Sc$_2$@C$_{84}$
which is considerably longer than the theoretical value of 1.43 Å [34], indicating some significant distortion of the polar regions of the C₈₄ cage. Such an anomalous large C–C distance [1.90(15) Å] has also been reported for the polymeric fullerene, RbC₆₀ [39]. The variety of thermal behavior of metal atoms inside the carbon cage found for Sc₂@C₈₄ and La@C₈₂, as well as La₂@C₈₀ in the next section, may lead to the discovery of novel physical properties of this type of material.

6

Two Sc Atoms in C₈₀

Out of the five Platonic solids, the cube, tetrahedron, and octahedron appear in crystals in nature. The other two solids, the dodecahedron and icosahedron, have been seen in fullerenes, proteins, and viruses. However, no such molecules or crystals having a double-shell Platonic solids shape have been discovered in nature. We found for the first time such an example in the total electron density distribution of La₂@C₈₀, i.e., a C₈₀ higher fullerene encapsulating two La atoms. A perfect pentagonal dodecahedron charge density is formed by two La atoms in an icosahedron Iₘ-C₈₀ cage [5]. This novel shape of the charge density has been observed as a result of a highly selective trajectory of the two La atoms hopping along the hexagonal rings of the Iₘ-C₈₀ polyhedral network.

The cell parameters are determined as a=18.2872(8) Å, b=11.2120(4) Å, c=11.1748(4) Å, and β=107.91(1)° (monoclinic: P2₁), by the Rietveld analysis. The reliability factor (R-factor) based on the Bragg intensities, R_p, and weighted profile R-factor, R_wRp, were 6.3 and 2.6%, respectively. The MEM charge density based on Rietveld analysis was derived with 502 observed structure factors by dividing the unit cell into 128×72×72 pixels. The reliability factor of the final MEM charge density was 3.8%.

The three-dimensional equi-charge density surface of the La₂@C₈₀ molecule is shown in Fig. 13. The equi-density level is 1.7 e/Å³. The obtained MEM charge density reveals six- and five-membered rings consistent with Iₘ symmetry of the C₈₀ cage. Figures 13a and 13b represent the top views along the S₁₀ and C₂ axis of

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**Fig. 12** a Equi-contour (2.5 e/Å³) MEM charge density distribution of Sc₂@C₈₄. b Schematic representation of the Sc–Sc, Sc–C, and C=C distances obtained from the MEM charge density.
A pentagonal dodecahedron cage, which should be due to the charge density of the encaged La atoms, is clearly recognized inside the C$_{80}$ cage. The inner dodecahedron cage is also shown separately in the figure. The calculated total charge based on the MEM results is 108.8(4) e, which is very close to the number of electrons of the triply charged state of two La$_3^+$ ions (108.0 e). The formal electronic structure is represented by (La$_3^+$)$_2$@C$_{80}^6$. The dodecahedral internal cage, therefore, represents a time-averaged trajectory of the motion of two La atoms encapsulated inside the C$_{80}$ cage.

The entire La$_2$@C$_{80}$ molecule possesses $I_h$ symmetry, the same as the empty $I_h$-$C_{80}$, since every pentagon on the dodecahedral charge density is faced with hexagonal rings of the C$_{80}$ cage. This is consistent with the previous $^{139}$La and $^{13}$C NMR studies, which suggests that the molecule has $I_h$ symmetry [40]. The observed longest La–La distance and the nearest La–C distance are 3.84(2) and 2.39(3) Å, respectively. These values can be compared with reported theoretical values (La–La; 3.665 Å and La–C; 2.56 Å) [41] for the $D_{2h}$-symmetry structure of La$_2$@C$_{80}$, in which La atoms are assumed to locate symmetrically with respect to the C$_2$ axis. The section of the charge density along the six-membered rings on the $I_h$-$C_{80}$ cage is shown in Fig. 14. The observed section of the internal dodecahedral cage is totally homogeneous in density. This indicates that the two La atoms, separated by 3.84 Å from each other, are hopping rapidly inside the round $I_h$-$C_{80}$ cage having a trajectory connecting the hexagonal rings of C$_{80}$ but not the
pentagons. This is a highly selective trajectory for the internal motion of the encaged La atoms, which has never been observed in any of the other metallofullerenes.

In the study, the $I_h$ symmetry constraint is restricted to the $C_{80}$ fullerene cage only in the Rietveld analysis. In the MEM analysis, the $I_h$ symmetry constraint of the $C_{80}$ fullerene was released and the lattice symmetry $P2_1$ was used as a constraint. Eventually, the MEM clearly exhibits the $I_h$ symmetric charge density features for two encapsulated La atoms as well as the $C_{80}$ cage under the $P2_1$ symmetry constraint. Because of the high symmetry of the $I_h$-$C_{80}$ cage, such a highly symmetrical charge density with a pentagonal dodecahedron shape has been realized for the encaged La atoms.

7

The Sc Dimer in IPR-Violated $C_{66}$

The isolated-pentagon rule (IPR) [42, 43], stating that the most stable fullerenes are those in which all pentagons are surrounded by five hexagons, has been considered as the most important and essential rule governing the geometry of fullerenes. In fact, all the fullerenes produced, isolated, and structurally characterized to date have been known to satisfy the IPR [16]. There are no IPR fullerenes possible between $C_{60}$ and $C_{70}$, and so the observation of any fullerenes in that range means the violation of the IPR. Shinohara et al. reported the first production and isolation of an IPR-violating metallofullerene, $Sc_2@C_{66}$, in 2000. Immediately after this, the IPR-violated structure of the fullerene was determined for the first time [6] using synchrotron radiation powder data by the MEM/Rietveld method [1, 9]. The result revealed that encapsulation of the $Sc_2$ dimer significantly stabilizes this otherwise extremely unstable $C_{66}$ fullerene.

The obtained powder data were analyzed by the MEM/Rietveld method. The space group and the rough lattice constant values were deduced from the powder pattern by using the powder-pattern-indexing computer program, DICVOL91 [44]. The average size of the fullerene molecule and the unit cell volume allowed us to presume the existence of two molecules in a unit cell. The central position of the fullerene cage and Sc atom positions were placed at 2a; (0, $y$, $z$) and 4a; ($x$, $y$, $z$) sites, respectively. Then, in the first pre-Rietveld analysis, a homogeneous spherical shell density, which would be the simplest model used in the previous Rietveld analysis, was used for the carbon cage structure model. By pre-Rietveld analysis of the MEM/Rietveld method, the $Sc_2@C_{66}$ crystal structure was determined as that of space group $Pmn2_1$ (No.31); $a=10.552(2) \text{ Å}$, $b=14.198(2) \text{ Å}$, $c=10.553(1) \text{ Å}$. Then, the radius of the fullerene sphere was refined as a structural parameter in the Rietveld refinement. As for the temperature factors, the isotropic harmonic model was used for the encapsulated metal atom: an isotropic Gaussian distribution is presumed for a Sc atom in the starting mode. The reliability factors ($R$-factor) based on the Bragg intensities, $R_b$, and weighted profile $R$-factor, $R_{wp}$, of the first pre-Rietveld fitting were $R_{wp}=5.6\%$ and $R_f=26.8\%$. The fitting result is shown in Fig. 15, in which some of the peaks in the lower angular region show, at this stage, large discrepancy between the calculated intensities based on the model and observed ones.
It is well known that the MEM can extract useful information purely from observed structure factor data beyond the presumed crystal structure model refined in the pre-Rietveld analysis. Following the pre-Rietveld analysis, MEM analysis was carried out by the computer program, ENIGMA [17]. The reliability factor of the MEM charge density based on the structure factors was 7.4%. The obtained charge density inserted in Fig. 15 clearly exhibits two highly concentrated density regions inside the carbon cage, which obviously correspond to the encapsulated Sc atoms. And the Sc charge density has already been overlapping with that of the carbon cage. In addition, the section of the carbon cage indicates the presence of the several local maxima.

Although there are a number of ways to violate the IPR, the most straightforward way to do this is to generate the so-called fused pentagon where pentagons are adjacent to each other. For 66-atom carbon cages with hexagonal and pentagonal faces, there are in total 4,478 possible (non-IPR) structural isomers with $2\times C_3$, $1\times C_{3v}$, $18\times C_{2p}$, $112\times C_2$, $211\times C_2$, and $4,134\times C_1$ symmetry [45]. Considering the observed 19 lines (5×2; 14×4) in the high-resolution $^{13}$C NMR spectrum of Sc$_2@C_{66}$ [6], only eight structural isomers of C$_{66}$ with $C_{2v}$ symmetry can satisfy this $^{13}$C NMR pattern. The structure models of isomers are shown in Fig. 16.

From the Sc atom positions in the MEM charge density, the cage orientation in the unit cell can be specified by the $C_2$ axis and mirror plane. Under the constraint of such $C_{2v}$ symmetry, the revised structure model for the next pre-Rietveld analysis was constructed based on the Sc atom positions in the MEM.
Fig. 16 Schematic structure models of eight $C_{60}$ isomers of $C_{60}$ fullerene
Fig. 17  Plot of reliability factors $R_{wp}$ and $R_I$ of the Rietveld refinements for the $C_{66}^+ C_{2V}$ isomers.

Fig. 18  Fitting result of the final Rietveld refinement with the MEM charge densities of the IPR-violating $Sc_2@C_{66}$ fullerene with top view along the $C_2$ axis and side view as the equi-contour (1.4 e Å$^{-3}$) surface. The two pairs of fused pentagons are clearly seen. The six- and five-membered-ring networks are superimposed on the charge densities. The contour lines of the inserted section of the MEM charge density are drawn from 0.0 to 3.0 e Å$^{-3}$ with 0.3 e Å$^{-3}$ intervals. The charge density at the Sc–Sc bond midpoint is 1.2 e Å$^{-3}$, which is a larger value than that of Si covalent bonding, 0.7 e Å$^{-3}$.
charge density. The two Sc atoms were placed in the mirror symmetry to the $C_2$ axis. Each of the eight isomers was tried as a cage structure model to fit with the observed powder pattern in the Rietveld analysis. In the present Rietveld analysis, the positions of carbon atoms were placed according to an ab initio optimized geometry [45, 46] by using refined positions of the central position of the $C_{66}$ molecule, and were not refined to avoid chemically meaningless deformation of the molecular structure by the least-square refinement. The reliability factors for the isomers of the Rietveld refinement are plotted in Fig. 17. The reliability factors for isomer 4348 present decidedly the smallest reliability factors, which were $R_{wp}=2.4\%$ and $R_f=13.1\%$. The result of the pre-Rietveld fitting is shown in Fig. 18. The fitting result has significantly improved the $R$-factors and showed the best fitting result in the analysis.

7.1 Charge Density of Sc$_2$@C$_{66}$

The MEM 3-D electron density distribution of Sc$_2$@C$_{66}$ based on the fitting result of Fig. 18 is shown in the same figure. The final MEM charge densities, whose reliability factor is $R_f=5.4\%$, clearly exhibit a pair of two-fold-fused pentagons on a $C_{66}$-C$_{2v}$ cage that encapsulate a Sc$_2$ dimer; the experimentally revealed Sc$_2$@C$_{66}$ structure has the least number and degree of fused pentagons out of the 4,478 possible isomers. The section of the charge density is also inserted in Fig. 18 as the contour map. In the map, the heavily overlapping charge densities were observed between Sc and Sc as well as Sc and carbon cage. This should indicate the existence of covalent bonding between the two Sc atoms as well as Sc and carbon cage.

The Sc$_2$@C$_{66}$ shown in Fig. 18 contains two pairs of two-fold fused pentagons to which the two Sc atoms are closely situated. The observed Sc–Sc distance is 2.87(9) Å, indicating the formation of a Sc$_2$ dimer in the $C_{66}$ cage. The intrafullerene electron transfers in endohedral metallofullerenes have been known to play crucial roles in stabilizing the metallofullerenes [47–49]. Since the obtained MEM charge density is the total electron density, the charge state of an encapsulated metal atom can be examined by counting the number of electrons around the metal-atom charge density [1, 9]. The charge state so determined corresponds to the number of electrons transferred from the metal atoms to the fullerene cage. The number of electrons in the area corresponding to Sc$_2$ dimer from the MEM charge density is 40.0(2) $e$, which is very close to that of (Sc$_2$)$_{2}^{2+}$ with 40 $e$, indicating that the Sc$_2$ dimer donates two electrons to the $C_{66}$ cage providing a formal electronic state of (Sc$_2$)$_{2}^{2+}@C_{66}$. It is this charge-transfer interaction between the Sc$_2$ dimer and the fused pentagons that significantly decreases the strain energies caused by the pair of fused pentagons and thus stabilizes the fullerene cage. The IPR is not necessarily a test for the stable geometry of endohedral metallofullerenes.

It should be noted that the recent theoretical study suggested a different structural model of Sc$_2$@C$_{66}$ based on the isomer 4059 [46]. The best fit of the Rietveld refinement based on this theoretical model gives the reliability factors $R_{wp}=9.1\%$ and $R_f=57.6\%$. The fitting result is shown in Fig. 19 with the structural model. The
Fig. 19  Fitting result of the Rietveld analysis for the structure model reported in Ref. [46] based on the isomer 4059. The inset is the molecular structure model of this analysis.

suggested longer Sc atom distance than that of the refined 4059 base Sc₂@C₆₆ structure caused a much worse reliability factor than those shown in Fig. 17. This extremely large discrepancy between the calculated and observed X-ray powder pattern should be caused by the burger-shaped cage structure of 4059 and the difference of the Sc–Sc interatomic distance.

Even at the Rietveld analysis level, it is concluded that the X-ray diffraction data obviously cannot be explained by the Sc₂@C₆₆ structure model based on 4059 isomer. In Sc₃@C₈₂ [7] and Sc₂@C₆₆ [6] each scandium atom donates one electron to the fullerene cage, whereas two electrons are transferred from each Sc atom to the fullerene cages in Sc@C₈₂ [3] and Sc₂@C₈₄ [4].

It seems that there is always one electron transfer from Sc to the fullerene cage (e.g., Sc₃@C₈₂ and Sc₂@C₆₆) when the encapsulated scandium atoms form a cluster. The published theoretical calculation [46] could not explain both the structure and the electron transfer of Sc₃@C₈₂.

Obviously, the currently existing theoretical calculations are not enough to treat such systems as metallofullerenes encapsulating metal clusters as well as metallofullerenes having covalent bonding character. To give a better understanding of the structures and electronic properties of these new types of endohedral metallofullerenes, further research and development of the well-refined theoretical methodology is highly required.
8

The Sc₃ Cluster in Sc₃@C₈₂

In the case of the trimetallofullerene, cluster formation of Sc atoms inside the carbon cage was revealed by the MEM/Rietveld analysis [7]. A section of the equi-contour surface of the MEM charge density for Sc₃@C₈₂ is shown in Fig. 20a. The carbon cage clearly exhibits a network of six- and five-membered rings. The three-leaves feature can be clearly seen inside the carbon cage. Sc₃@C₈₂ is concluded to be an endohedral metallofullerene encapsulating a triangular Sc trimer inside the C₃ᵥ -C₈₂ cage. The contour map of a section disecting the three leaves is shown in Fig. 20b, which reveals the presence of three density maxima in the feature. By accumulating a number of electrons around the Sc atoms in the MEM density, the number of electrons around the maxima is found to be 60.2(3) e, which is very close to that of the triply charged state of a scandium cluster, Sc₃³⁺ (60.0 e). The schematic representation of a Sc₃@C₈₂ molecular section corresponding to Fig. 20a is shown in Fig. 20c.

Previous experimental [3, 4] and theoretical [34, 35] studies indicated that the charge state of mono- and discandium metallofullerenes such as Sc@C₈₂ and Sc₂@C₈₄ is 2+, leading to the Sc²⁺@C₈₂ and (Sc²⁺)₂@C₈₄ configurations, respectively, owing to intrafullerene electron transfer from Sc atom(s) to the fullerene cages. In contrast, the total charge state of the Sc trimer in Sc₃@C₈₂ derived from the MEM charge density is Sc₃³⁺, which differs considerably from those of Sc@C₈₂ and Sc₂@C₈₄. Upon encapsulation, three outer electrons of Sc₃ are transferring to the C₃ᵥ-C₈₂ cage, resulting in the electronic configuration as described by Sc₃³⁺@C₈₂. The determined structure can also provide a rationale for the former ESR results that the three Sc ions should be geometrically equivalent inside the C₈₂ cage [50–53].

The finding of the presence of a trimer form of Sc₃³⁺ in the fullerene cage, rather than that of three mutually separated Sc²⁺ ions, is somewhat unexpected in the light of the discandium (Sc²⁺)₂@C₈₄ fullerene [4], where the two individual Sc²⁺ ions are separated by 3.9(1) Å in the C₈₄ cage. Obviously, the formation of the Sc₃³⁺ trimer should be much more energetically favorable than that of three.

![Fig. 20](image-url)

**Fig. 20** a Equi-contour (2.1 e/Å³) density map of the MEM charge density of the half section of Sc₃@C₈₂. The C₃ᵥ axis is almost perpendicular to the figure plane. b MEM charge density of the (100) section. Contour lines are drawn from 0.0 to 6.0 e/Å³ with 0.3 e/Å³ intervals. c Schematic representation of the structure model of Sc₃@C₈₂ corresponding to figure a.
mutually separated Sc$^{2+}$ ions, (Sc$^{2+}$)$_3$, entrapped in a subnanoscale space with the average inner diameter of 5.3 Å provided by the $C_{3v}$-$C_{82}$ fullerene. The possibility of Sc$_3$ cluster formation in Sc$_3@C_{82}$ was suggested previously based on the ESR [51, 52] and theoretical [21, 54] studies. The X-ray results have revealed a detailed endohedral nature as well as encaged Sc$_3$ structures for Sc$_3@C_{82}$.

In Fig. 21, the schematic representations of the final structure model are shown according to the structure parameters determined by the Rietveld analysis. As shown in Fig. 21a, the Sc$_3$ trimer does not reside at the center of the carbon cage but is close to the triply fused hexagonal part (not to the center of a hexagon at the other end) along the $C_3$ axis. The nearest distance between the center of the Sc$_3$ trimer and carbon atoms and the nearest neighbor Sc–C distance obtained from the MEM map are 3.4(1) and 2.52(2) Å, respectively. Furthermore, it shows that the Sc trimer is at rest in the cage even at room temperature.

**Fig. 21 a, b** Schematic representation of the structure model determined by the MEM/Rietveld method; a and b are the side and top views, respectively

**9 Sc$_2$C$_2$ Molecule in C$_{84}$**

Up to 1999, only metal atoms [1–5], metal clusters [6, 7], metal nitrides [55–57], and noble gas atoms [58–60] were observed to be encaged inside C$_{60}$, C$_{70}$, or various sizes of higher fullerenes. The experimental evidence for carbon atoms or metal–carbon compounds (carbides) being encapsulated inside fullerenes had not yet been observed. In 2000, Shinohara et al. succeeded in the first production, isolation, and spectroscopic characterization of a scandium carbide endohedral fullerene (Sc$_2$C$_2$)$_3$@C$_{84}$. Following this, the first experimental evidence based on synchrotron X-ray diffraction was presented and revealed that the Sc carbide is encapsulated in the form of a lozenge-shaped Sc$_2$C$_2$ cluster inside the $D_{2d}$-C$_{84}$ fullerene [8].

The X-ray powder data were measured by the large Debye–Scherrer camera at SPring-8 BL02B2 using solvent-free (Sc$_2$C$_2$)$_3$@C$_{84}$ powder sample. The exposure time on the IP was 80 min. The wavelength of incident X-rays was 0.75 Å. The
X-ray powder pattern of \((\text{Sc}_2\text{C}_2)@\text{C}_{84}\) was obtained with a 0.02° step from 3.0° to 30.5° in \(\theta\), which corresponds to 1.45 Å resolution in \(d\)-spacing. The obtained powder pattern was identified as that of a fcc crystal. The space group of the present crystal is assigned to be \(Fm\bar{3}m\), which is cubic \([a=15.8644(4)\ \text{Å}]\).

The experimental data were analyzed by the MEM/Rietveld method with the 36 structure factors. The reliability factors in the process of pre-Rietveld analysis for MEM/Rietveld analysis are \(R_i=2.4\%\) and \(R_{wp}=2.1\%\), which are the best value among those for the other metallofullerenes. Eventually, the MEM analysis was carried out by the computer program ENIGMA using 128×128×128 pixels for a unit cell. The reliability factor of the MEM charge density is \(R=1.7\%\). In the charge density, several density maxima were found inside the carbon cage.

From the charge densities inside the fullerene cage, the four internal maxima are identified as Sc and C atoms. This provides the direct experimental evidence for encapsulation of the \(\text{Sc}_2\text{C}_2\) carbide cluster in the \(\text{C}_{84}\) cage. The MEM charge density also reveals that the \(\text{C}_{84}\) cage has \(D_{2d}\) (No.23) symmetry and that the \(C_2\) axis is parallel to the \(<100>\) fcc direction of the unit cell. Due to the site symmetry of 4 mm, the \(C_2\) axis of the \((\text{Sc}_2\text{C}_2)@\text{C}_{84}\) molecule is oriented to six equivalent \(<100>\) directions showing a merohedral disorder. Since Fig. 22a exhibits the section of the Sc atoms and C atoms at four positions among six equivalent positions, it is concluded that the \(\text{Sc}_2\text{C}_2\) cluster is encapsulated in a \(D_{2d}\)-\(\text{C}_{84}\) fullerene cage. By stereochemical consideration, the possibility of a linear \(\text{Sc}–\text{C}–\text{C}–\text{Sc}\) cluster is ruled out for the structure of the \(\text{Sc}_2\text{C}_2\) cluster, since the nearest Sc–C distance, 1.5 Å, of a linear \(\text{Sc}–\text{C}–\text{C}–\text{Sc}\) cluster is much shorter than the existing Sc–C distances of any molecules. The determined molecular structure is shown in Fig. 22b.

**Fig. 22** a Half section of the equi-contour \((1.9 \text{ e/Å}^3)\) surface of the MEM charge density for \((\text{Sc}_2\text{C}_2)@\text{C}_{84}\). The cross section corresponds to the \((100)\) plane. The \(\text{Sc}_2\text{C}_2\) cluster is emphasized by dotted lines. In the cubic symmetry, the \((\text{Sc}_2\text{C}_2)@\text{C}_{84}\) molecules exhibit merohedral disorder in the unit cell. Thus, an \(\text{Sc}_2\text{C}_2\) cluster represents the disordered feature along \(<100>\) directions with respect to the fullerene cage. b Schematic representation of the \((\text{Sc}_2\text{C}_2)@\text{C}_{84}\) molecule determined by the MEM/Rietveld method. The observed C–C distance, 1.42(6) Å, is between a typical single and double bond of alkenes and very close to the C–C bond (1.43 Å). The Sc–C distance, 2.26(3) Å, shows reasonable agreement with an ab initio theoretical Sc–C bonding distance (2.135 Å) of the ScC2 cluster.
The resultant Sc–Sc and C–C distances of the Sc₂C₂ cluster are 4.29(2) and 1.42(6) Å, respectively. The observed C–C distance is somewhere between a typical single and double bond of alkenes, and very close to C–C bonds (1.43 Å) which connect two pentagons on a C₆₀ molecule [55]. Moreover, the Sc–C distance is 2.26(3) Å, which shows reasonable agreement with an ab initio theoretical Sc–C bonding distance (2.135 Å) of the ScC₂ cluster [61–63]. The number of electrons belonging to the Sc₂C₂ cluster is estimated to be 51.9(2) e from the MEM charge density, indicating that the Sc₂C₂ species is in a divalent charge state in the C₈₄ fullerene cage. The formal electronic structure of (Sc₂C₂)@C₈₄ can thus be described as (Sc₂C₂)²⁺@C₈₄⁻. The ab initio calculation on the ScC₂ cluster indicated that the nature of the chemical bonding between Sc and C₂ is highly ionic, which is due to a σ-donation and π-back-donation scheme.

10 Conclusion

From the structural studies given in this article, it is evident that the charge density study by the MEM/Rietveld method using SR powder diffraction data is powerful for determination of the endohedral nature of metallofullerenes. There is no doubt the structural information provided greatly contributes to progress in research of endofullerenes as well as endofullerene peapod, which is the metallofullerene-encapsulating carbon nanotube.

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Polymeric Fullerene Phases Formed Under Pressure

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Abstract Fullerenes, in particular C_{60}, can form covalent intermolecular bonds (“polymerize”) when treated at high temperature under high pressure. This contribution briefly reviews some recent advances in this field. Short overviews are given of the pressure–temperature phase diagrams of pristine C_{60} and C_{70} and of their physical properties under high pressure. The paper has its main emphasis on the structures and properties of the one- and two-dimensional (chains and planes) polymeric phases of C_{60} created in the range 1–9 GPa (10–90 kbar) and up to 1100 K. Their structures, as obtained from studies on polymerized single crystals, the treatment conditions used to obtain well-defined structures, and some selected physical properties, including the surprising discovery of ferromagnetism, are discussed. The paper presents the results of both ex situ and in situ structural studies. Three-dimensional polymers, and the possibility to create well-defined three-dimensional structures by high-pressure treatment of low-dimensional polymers, are also discussed. Finally, a short section devoted to higher fullerenes discusses the polymeric forms of C_{70}, including the ordered zigzag chain phase recently created under hydrostatic pressure conditions.

Keywords High pressure · Fullerene polymers · Lattice structures · Raman spectroscopy · Intermolecular bonding

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Abbreviations

\[ \Delta \] Difference in energy between molecular orientations
\[ \gamma \] Grüneisen parameter
\[ \omega \] Vibrational frequency
\[ E \] Band gap energy
\[ E_a \] Activation energy for polymer breakdown
\[ f \] Fraction of molecules with “pentagon” orientation
\[ fcc \] Face-centered cubic
\[ hcp \] Hexagonal close-packed
\[ p \] Pressure
\[ rhh \] Rhombohedral
\[ sc \] Simple cubic
\[ T \] Temperature
\[ T_g \] Glass transition temperature of C\textsubscript{60}
\[ T_0 \] Rotational transition temperature of C\textsubscript{60}
\[ V \] Volume

1 Introduction

The two “classical” allotropes of carbon, graphite and diamond, have been known for thousands of years, but it is only just over 200 years since Smithson Tennant showed that diamond is a form of pure carbon, and only 50 years since graphite was first converted into diamond [1] using a process requiring a high temperature, a suitable catalyst, and, most important, high pressure. Although the graphene sheets in graphite are extremely strong and incompressible, even comparatively low pressures can cause large changes in the structure of graphite and its intercalation compounds [2] because the weak bonds in the direction perpendicular to these sheets make bulk graphite quite compressible.

The various forms of molecular carbon, such as fullerenes and carbon nanotubes, share a similar structural feature. The molecules themselves are incompressible, but the intermolecular interactions are weak and similar to those in graphite. Again, pressure may induce large structural changes. Near room temperature the equilibrium phase line between graphite and diamond falls near 2 GPa [3], and in principle a diamond would transform into graphite if kept for an infinite time just above this pressure. Applying pressures of a similar magnitude to carbon nanotube bundles leads to strong radial deformations (polygonization)
[4, 5] and even collapse. Although no such deformation effect has been observed in the quasi-spherical fullerene molecules, fullerene solids may also suffer large structural changes at rather low pressures. This was first observed by Aoki et al. [6], who studied the Raman and IR spectra of solid C_{60} under high pressures at room temperature. Spectra from samples recovered from a pressure of 5 GPa showed a number of new lines, interpreted as arising from a decrease in lattice symmetry. Later, Iwasa and coworkers [7] showed that high-temperature treatment under high pressure led to the formation of at least two new structural phases. It was already known that covalent intermolecular bonds could be formed in C_{60} by irradiation with visible light [8], and it was soon realized that the same feature was shared by these new high-pressure phases. Such materials, in which basically intact fullerene molecules are linked by covalent bonds, are now commonly known as fullerene polymers, or polymeric fullerenes.

This contribution briefly reviews the structures and properties of polymeric fullerene phases formed under pressure. Space being limited, the review will have a strong emphasis on the low-dimensional structures formed in C_{60} below about 9 GPa, an area where great progress has been made over the last five years. The basic properties and structures of solid fullerenes will be assumed known from other chapters in this volume or from other general overviews [9–11], but to set the background parts of this chapter will be devoted to the effect of pressure on molecular fullerenes (a term which here implies that no covalent intermolecular bonds exist) and to fullerene polymers created without the help of high pressure. A few comprehensive reviews of fullerenes under high pressure have already appeared in the literature [12–15] but the pace of progress is very rapid and several recent subjects, for example the discovery of magnetic carbon [16] and the results of in situ polymerization studies [17–19], have not been discussed before. Readers unfamiliar with high-pressure technology and techniques are referred to recent specialized literature [20, 21] for more information.

2 Molecular Fullerenes Under Pressure

2.1 Effects of Pressure Media

When carrying out experiments under high pressure, here defined as pressures exceeding 100 MPa (1 kbar), it is important to choose a suitable pressure-transmitting medium. Solid pressure media are easier to use than fluids (liquids or gases) but always introduce an anisotropy in the applied pressure. Many recent studies show that the application of an anisotropic pressure may give significant effects on the morphology, structure, or texture of any polymeric phases produced, irrespective of whether polymerization was initiated by the pressure treatment itself [22–27] or by electron doping [28]. Strong shear stress also seems to promote the polymerization process, and mechanical milling has been reported to lead to polymerization of C_{60} even at atmospheric pressure [29]. To get accurate and repeatable data, fluid pressure media should thus be used whenever possible, to create truly hydrostatic conditions. Rare gases are usually considered “ideal”
media, being chemically inert, optically transparent, electrically insulating, and fluid over large ranges of temperature and pressure [20, 21]. However, in the lattices of solid fullerenes the interstitial spaces are large enough to accommodate both rare gas atoms and many small molecules at and above room temperature. Many liquids and gases thus easily form intercalation compounds with fullerenes, which makes them unsuitable as pressure media [13, 14, 30]. Being rather “soft” solids, fullerenes are often studied without adding any additional pressure medium, i.e., the load is applied directly on the sample material itself. This may be quite acceptable at high pressures, but studies at low pressures (p<1 GPa) often show large differences between results obtained under hydrostatic and nonhydrostatic conditions [13].

### 2.2 Orientational Phase Diagrams of C\(_{60}\) and C\(_{70}\)

Before discussing the formation and structures of polymeric fullerenes we briefly review what happens to molecular C\(_{60}\) and C\(_{70}\) when pressure is applied.

At low pressure, including atmospheric pressure, C\(_{60}\) has three structurally different phases [9–11]. Above \(T_0=260\) K, the molecules form a rotationally disordered face-centered cubic (fcc) lattice with symmetry group Fm3m. At very high temperatures the molecules rotate freely, but with decreasing temperature there is an increasing correlation between the rotational movements of neighboring molecules. On cooling through \(T_0\), a primitive cubic or simple cubic (sc) phase (symmetry group Pa3) is obtained, accompanied by a decrease in volume \(V\) by about 1% [9, 13]. Although the quasi-free molecular rotation has stopped in this phase, the molecules can still ratchet between a small number of orientational states and the orientational order will change with temperature. On further cooling molecular motion becomes very slow, and below the glassy crystal transition (or glass transition) at \(T_g=90\) K the orientational disorder becomes constant (“orientational glass”). Both \(T_0\) and \(T_g\) increase with pressure, with slopes \(dT_0/dp=160\) K GPa\(^{-1}\) and \(dT_g/dp=62\) K GPa\(^{-1}\), respectively [13], such that at 290 K the fcc–sc rotational transition is observed to occur at 0.19 GPa.

There are two possible molecular orientations in the sc phase, here descriptively denoted the P (pentagon) and H (hexagon) orientations. This notation arises because a double bond on one molecule can be oriented toward a carbon-atom pentagon or a hexagon on its neighbor [9–11]. Quite advanced theoretical models have been developed for the orientational interactions and dynamics [9–11, 31], but to a first approximation we can assume simply that the relative fraction \(f\) of P oriented molecules is

\[
f(T) = \frac{1}{1 + \exp \left(-\Delta/k_BT\right)}
\]

where \(\Delta\) is the difference in energy between the states. At atmospheric pressure the energy of the P-oriented state is 12 meV lower than that of the H-oriented state, and on cooling \(f\) will increase from about 60% near 260 K to almost 85% at \(T_g\) [9–11]. However, an applied pressure will change the sign of \(\Delta\), and David and Ibberson [32] showed that at 150 K this occurs at a pressure of 191 MPa as shown in Fig. 1. As a consequence, a fully H-oriented phase may exist at low tempera-
tures under high pressure. If $\Delta(p, T)$ is known, $f$ can be calculated for any temperature and pressure in the sc phase, using Eq. 1. As a first approximation we can assume that $\Delta$ is independent of temperature, $T$, but linear in pressure, $p$, as $\Delta=a+bp$, where the constants $a$ and $b$ can be found from the results of David and Ibberson (Fig. 1b). In this case, $f$ will be constant on straight lines in the pressure–temperature phase diagram as shown by the dotted lines in the orientational phase diagram in Fig. 2. (This model is not necessarily very accurate since $\Delta$ should depend on $V$ rather than $p$; near 100 K lower equilibrium pressures near 0.15 GPa are found [13], indicating that $\Delta$ indeed depends slightly on $V$ and/or $T$.) Figure 2 shows coordinates corresponding to 30, 50 (vertical line), 65, 80, and 92% H-oriented molecules. The last number corresponds to the case when, on average, 11 out of 12 molecules are H oriented. Burgos et al. [33] have calculated

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**Fig. 1** a Fractional occupancy of the P-oriented state of $C_{60}$ as a function of pressure, and b difference in free energy between the P and H oriented states, both at 150 K. Reprinted with permission from: WIF David and RM Ibberson, “High-pressure, low-temperature structural studies of orientationally ordered $C_{60}$”, J. Phys.: Condens. Matter vol. 5 (1993) 7923–28 [32]. Copyright © 1993 Institute of Physics Publishing Ltd
the intermolecular orientation potential for a C\textsubscript{60} molecule surrounded by 12 neighbors in a lattice. With all neighbors P oriented there were two local energy minima, corresponding to the P and H states, respectively, but when all neighbors were H oriented there was only one stable (H) orientational state. Orientational defects are thus allowed in a preferentially P-oriented phase but not in an H-oriented structure, and it is possible that a final, sudden transition into an H-oriented state occurs at some critical value of \( f \) when the intermolecular potential forces all molecules into the stable H orientation [13]. Small anomalies have indeed been observed in many properties of C\textsubscript{60} in the range 1.3–2.4 GPa [13], where more than 90% of the molecules should be H oriented.

It should be noted here that many very-high-pressure experiments still show the presence of a fcc lattice, with no indications of orientational order. Such experiments often use anvil devices and/or solid pressure media, and the observation of orientational disorder might possibly be a result of “quenching” the original zero-pressure structure by rapid pressurization.

If the lattice is expanded instead of compressed the P orientation is favored, and an almost completely P-oriented lattice has indeed been observed in C\textsubscript{60} expanded by intercalation of CO [34]. However, this increase in orientational order is at least in part due to an electrostatic host–guest interaction.

Crossing the glass transition line in Fig. 2 from above, the existing orientational structure becomes “frozen in”, i.e., independent of further changes in pressure or temperature within the low-temperature glass phase region. Very interesting relaxation effects can therefore often be observed when heating back through the glass transition. Indeed, if the pressure has been changed at low temperature, \( T_g \) on heating differs from that given by the glass transition line in Fig. 2 because the reorientation changes the molecular volume [13, 35].

For C\textsubscript{70} the phase diagram is more complicated. Because of the anisotropic molecules it should contain at least three phases, with free molecular rotation at high temperature, uniaxial rotation at intermediate temperatures, and frozen rotation or

![Fig. 2](image-url) Approximate pressure–temperature phase diagram showing the boundaries between the three phases of molecular C\textsubscript{60}. Dashed lines in the simple cubic field show coordinates corresponding to 30, 50, 65, 80, and 92% H-oriented molecules.
ratcheting at low temperature. Also, C_{70} may have either a hexagonal close-packed (hcp) or fcc structure at high temperature [9], and most real crystals contain both since the structures differ only in their stacking sequences. The two types of lattice evolve differently with temperature, and several transitions can often be observed. It has been observed that C_{70} always returns to the fcc structure after high-pressure treatment [36], suggesting that this phase is more stable. From the fcc phase, C_{70} transforms on cooling into a rhombohedral (rhh) structure with uniaxial rotation near 355 K, and then to an orientationally ordered phase below 280 K [37].

Because the structure is not well known even at atmospheric pressure, the $p$–$T$ phase diagram of C_{70} is uncertain. Figure 3 shows a tentative orientational phase diagram deduced from X-ray, thermal conductivity, compressibility, and spectroscopic data [13, 14, 38], assuming a fcc structure with free rotation at high temperature. Cooling freezes the quasi-free rotation, transforming molecular motion into uniaxial rotation, and on compression the molecular axes line up in the $\langle 111 \rangle$ direction of the crystal to minimize the volume. Further cooling may then create an orientationally ordered phase at low temperature. For hcp crystals, however, the low-pressure diagram may be significantly different.

### 2.3 Physical Properties of Molecular Fullerenes Under Pressure

Detailed reviews of the physical properties of fullerenes under pressure already exist [13, 14] and only a few important parameters will be discussed here. Since fullerene molecules have been found to be very incompressible the primary effect of high pressure is to decrease the intermolecular distance, which leads to changes in most physical properties. To a first approximation, solid molecular fullerites can be described as “three-dimensional graphite”, in the sense that the molecular interaction is similar to the interlayer interaction in graphite, and because compression can occur in three dimensions the bulk modulus $B$ is close to one third of that of graphite. However, the molecular reorientation from a P-oriented to an H-oriented structure with increasing pressure leads to anomalies.
in \( B \) because the latter structure has a lower volume per molecule. A recent review [14] discusses available experimental data, including the temperature and pressure dependence of \( B \) in both \( C_{60} \) and \( C_{70} \), and recommends zero-pressure limiting values \( B(0) \) for \( C_{60} \) at 290 K of 9.6 GPa in the fcc phase and 9 GPa (extrapolated to zero pressure) in the sc phase. In both structures \( B \) increases rapidly with increasing pressure as the intermolecular interaction increases.

Because the intramolecular bonds are strong and the intermolecular ones weak, different properties will be affected in different ways by high pressure. This is particularly clear for properties determined by the vibrational spectrum. The low-frequency acoustic and librational modes in the crystal should be quite sensitive to pressure, while the high-frequency intramolecular modes should not. This is also observed in experiments [13, 14]. Figure 4 shows the generalized density of states for low-frequency lattice modes of \( C_{60} \) at atmospheric pressure and 0.5 GPa (5 kbar) [39]. On average, the phonon energies shift upwards by about 0.32 GPa\(^{-1}\), corresponding to a large Grüneisen parameter \( \gamma = -\frac{d(\ln \omega)}{d(\ln V)} \approx 3.6 \). For comparison, Fig. 5 shows measured Grüneisen parameters for IR- and Raman-active intramolecular modes in \( C_{60} \) and \( C_{70} \) [40], which are all more than an order of magnitude smaller.

Solid molecular fullerenes are semiconductors with band gaps of 1.5–2 eV [9]. Compression increases the overlap of electron states between molecules, broadening the electron bands and decreasing the band gaps. Optical studies on \( C_{60} \) show that the gap energy \( E \) decreases nonlinearly with increasing pressure. The initial rate is \( \frac{dE}{dp} = -0.14 \text{ eV/GPa} \), decreasing to \(-0.02 \text{ eV/GPa} \) above 10 GPa [41]. Similar results are found for \( C_{70} \) [42]. Since theoretical calculations [43] agree well with these results, the pressure dependence of the band gap seems well understood.

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*Fig. 4* Phonon density of states at 180 K for the low-frequency modes of \( C_{60} \) at atmospheric pressure and at 0.5 GPa. Reprinted with permission from: H Schober and B Renker, “Pressure dependence of the external mode spectrum of solid \( C_{60} \),” Phys. Rev. B vol. 59 (1999) 3287–90 [39]. Copyright © 1999 The American Physical Society
Polymerized Fullerenes

3.1 Polymerization Without an Applied Pressure

Intermolecular bonds between fullerene molecules were first identified by Rao et al. [44, 45] after exposure of C₆₀ to strong visible light (“photopolymerization”), and they suggested that such bonds formed through a (2+2) cycloaddition mechanism. After optical excitation, one double bond on each of two neighboring molecules can break up and two single C–C bonds form between the molecules to create an intermolecular four-membered carbon ring. Experimentally, this is found to be the most common type of intermolecular bond structure in undoped fullerene polymers. Although the bonds have a very strong sp³-type hybridization, they are much weaker than typical “diamond-like” bonds, and many C₆₀ polymers, including the photopolymer, break down into separate, intact molecules on heating to 450–600 K.

Polymeric fullerene materials can be obtained by many methods, for example by irradiation with electrons or ions, treatment in a plasma generator, doping with alkali metals [9, 28, 46], direct chemical synthesis [47], or mechanical milling [29]. Because of the small penetration depth of light fullerenes can only be photopolymerized as thin films, but bulk photopolymer can be obtained by polymerization in solution [48, 49]. Diffraction studies show that photopolymers usually have a disordered fcc structure. Although some ordered films have been

Fig. 5 Mode Grüneisen parameters for IR- and Raman-active intramolecular modes in C₆₀ and C₇₀. Squares – Raman data for C₆₀, dots – IR data for C₇₀, open circles – Raman data for C₇₀.

observed [50], it is uncertain whether these are intrinsic or produced by inter-
action with the film substrates. Radiation-induced polymerization is basically
random and relies on molecular rotation to bring an excited bond in sufficiently
close contact with another molecule [45, 51], and photopolymerization thus
proceeds very slowly in the sc phase below 260 K. Photopolymers produced at
high temperature are believed to consist mainly of dimers, C_{120} [49, 50, 52], but
at room temperature larger clusters are formed. Optical spectroscopy indicates
that each molecule is bound to one to three other molecules [53, 54], and the
structures formed might thus be chains, branched chains [53], or rings with three
or more molecules [54]. However, XPS studies indicate that bonds may be formed
with up to six other molecules in saturated polymers, creating two- or three-
dimensional networks [55].

Photopolymerization of C_{70} is also possible, but because only five C=C bonds near
the “poles” of the molecule have a reasonable reactivity, the polymer yield is smaller
than for C_{60} and cluster size seems limited to mainly dimers, C_{140}, and trimers [56].

Photopolymerization can only be carried out in the absence of oxygen, since
the necessary triplet state in C_{60} is quenched by an interaction with O_2 [45, 51].
However, if C_{60} is irradiated for a long time in the presence of O_2 another toluene-
insoluble phase can be obtained. This phase, which is often termed “phototrans-
formed C_{60}” to distinguish it from the pure polymer, probably consists of oxidized
C_{60} in which intact or opened molecules are linked into large clusters by oxygen
bridges [45]. In contrast to the photopolymer, which readily reverts to free C_{60}
molecules on heating, the molecules in phototransformed C_{60} are permanently
damaged.

3.2 Polymerization of C_{60} Under Pressure

Under high pressure, a second pathway for polymerization is opened. Irradiation
with light still results in the formation of a disordered photopolymer, but coval-
ent bonds can also be formed without optical excitation, and the corresponding
reaction rate increases significantly at elevated temperatures. As a starting point
for this section we take Fig. 6, which is an adaptation of the “reaction map” for C_{60}
given by Blank et al. [12]. Symbols show pressure–temperature coordinates corres-
ponding to selected high-pressure experiments on C_{60} reported in the literature
up to 1997. At each point, C_{60} has been treated for a certain time (usually minutes
or seconds under extreme conditions, or up to hours near ambient conditions),
then quenched back to room temperature before the pressure has been released.
The structures observed after this treatment are indicated on the map, and it is
obvious that this reaction diagram contains a large number of structural phases.
The question whether these are stable structures, quenched intermediate tran-
sition states, or possibly experimental artifacts can only be answered by in situ
studies, and only recently have a few such studies been carried out. Some of the
phase boundaries in Fig. 6 have been replotted and differ slightly from those
given by Blank et al. [12].

The low-dimensional structural phases formed between 1 and 6 GPa [12–14]
have been well characterized, and their general structures were understood early
Fig. 6 “Reaction map” for C\textsubscript{60} (adapted from \[12\]) showing the structural phases obtained after short-term treatment under the conditions shown

[57]. As shown in Fig. 7, linking nearest neighbors in a fcc lattice can lead to at least three simple structures. One of these consists of one-dimensional linear chains running in the (110) direction. Two-dimensional sheets of linked molecules can form in two ways: either nearest neighbors in the (100) plane are bound together into squares, or the molecules in the close-packed (111) plane form a trigonal polymer sheet. Looking at a molecular model (or a standard soccer ball) it is immediately obvious that the intermolecular bonds (the rings of four carbon atoms forming the bonds) of a linear chain should all lie in the same plane. This is equally true for bonds along a single direction in the two-dimensional phases, but the plane of the bonds (or rings) need not coincide with that of the polymer sheet. In the square ring, the intermolecular bond is in the plane of the ring (“horizontal”) in one direction but at right angles to this (“vertical”) in the other. In the trigonal structure the intermolecular bonds lie in three different planes, all rotated by approximately 20° (depending on the geometrical distortion of the molecule) relative to the plane of the polymer sheet.

Since the three low-dimensional structures are well characterized the discussion will start with these, before turning to the less well understood three-dimensionally connected polymers obtained under more extreme conditions.
3.2.1.1 Orthorhombic (Linear-Chain) Phase

As mentioned in the Introduction, early high-pressure studies by Aoki et al. [6] and others at room temperature showed indications of polymerization above about 5 GPa, while Iwasa et al. [7] found that heating under similar pressures resulted in a practically complete polymerization. Such high pressures are not necessary for polymerization, however. Soon afterwards, Bashkin et al. [58] measured the compressibility of C$_{60}$ above room temperature and found a large, rapid change in volume at pressures near 1 GPa. This volume drop arises from the formation of covalent bonds between molecules, which decreases the intermolecular distance by almost ten percent. The polymerization reaction was reversible above about 500 K. From Fig. 8, which shows the location of the volume anomalies observed, it is clear that the hysteresis was very small at 700 K but increased rapidly on cooling, until near 450 K the polymeric phase was metastable to atmospheric pressure. (The sample polymerizes on entering the upper right area in the figure, while the polymer breaks down if heated into the area on the upper left.) The lowest observed polymerization pressure, just below 0.7 GPa, was observed near and above 500 K, and the “equilibrium line” for this first-order transformation extrapolates to approximately 300 K at atmospheric pressure. The
polymeric material obtained had a very disordered structure but was, of course, a bulk material, in contrast to the photopolymerized films created earlier. The first NMR studies on such pressure-polymerized material showed clear signatures of covalent sp$^3$ intermolecular bonds [59, 60], proving without doubt that such bonds existed in the material.

The dominant structural feature in C$_{60}$ polymerized at such low temperature and pressure is the formation of dimers or linear chains of C$_{60}$ molecules, as shown on the left side in Fig. 7. Such one-dimensional chains are formed below about 700 K over a very wide range of pressures, from about 0.7 GPa to at least 9 GPa, and probably higher. Since chains should form between nearest neighbors along the original ⟨110⟩ directions in the crystal, the decrease in intermolecular distance on polymerization distorts the original cubic lattice into an orthorhombic one. In comparison with the two-dimensional structures also shown in Fig. 7, the number of intermolecular bonds is fairly low, in agreement with the intuitive prediction that treatment under near-ambient conditions should give the smallest changes to the original structure. It is clear from Fig. 8 that both high pressure and an elevated temperature are necessary for the polymerization reaction to occur, since the higher pressure, or “polymerization”, branch of the phase line actually curves away to higher pressures as the temperature is lowered below 500 K. Although the dashed “equilibrium” line in Fig. 8 should always be approximately correct, both polymerization and depolymerization are thermally activated processes and the two phase lines shown in Fig. 8 are thus valid only over the timescale of this particular experiment. Polymerization has also been observed to occur at lower pressures and/or temperatures, but with a much slower reaction rate [59, 61].

Many studies have been carried out on polymerization of C$_{60}$ in the low-temperature range at pressures up to 9 GPa. The most detailed information about the

![Fig. 8](image-url)  
*Fig. 8* Low-pressure phase diagram for C$_{60}$ deduced from compression studies. Full curves show observed polymerization and depolymerization coordinates and dashed line the “equilibrium” line. The fcc–sc phase boundary is also shown, for comparison. Reprinted with permission from: IO Bashkin, VI Rashchupkin, AF Gurov, AP Moravsky, OG Rybchenko, NP Kobelev, YM Soifer, and EG Ponyatovskii, “A new phase transition in the T–P diagram of C$_{60}$ fullerite”, J. Phys.: Condens. Matter vol. 6 (1994) 7491–98 [58]. Copyright © 1994 Institute of Physics Publishing Ltd
lattice structure of the orthorhombic linear-chain phase formed in this region has been obtained from X-ray studies on single crystal C₆₀, polymerized for 5 h under hydrostatic pressure in silicone oil at 1.2 GPa and 570 K by Moret et al. [62]. Processing under such “gentle” conditions leaves the crystals macroscopically intact, but after treatment the crystals contained a mosaic of oriented domains (variants) with an orthorhombic structure. In each domain, the orientation of one of the original close-packed planes is preserved, but chains in different domains run in different, basically random directions approximately corresponding to (110) directions in the original fcc crystals. In this experiment the domains were large enough (>20 nm) that the diffraction pattern was limited by the instrumental resolution, and X-ray diffraction studies showed that the lattice parameters a, b, and c equalled 0.914, 0.99, and 1.466 nm, respectively, under ambient conditions. The chains run along the a direction, and the small intermolecular distance in this direction agrees well with calculations of the bond lengths formed by (2+2) cycloaddition. The basic structure thus agrees well with early predictions.

Closer analysis showed, however, that the rotational orientation of the chains is different from that suggested in early works. Núñez-Regueiro et al. [57] naturally assumed that the plane of the intermolecular bonds would be parallel to a lattice vector, resulting in an Immm symmetry, and making a further polymerization into the two-dimensional square sheet structure very easy. An analysis of the single-crystal diffraction patterns showed that this is not the case, and that the chains are rotated a small angle with respect to the lattice vectors. This is illustrated in Fig. 9, showing views of the C₆₀ molecules along the chains [62]. The planes of the four-carbon-atom rings in the bonds are indicated for three different rotation angles of the chains, 0°, 29°, and 45°. The rotation of the chains reduces the symmetry of the lattice from Immm to Pmnn [62]. Unfortunately, the resolution of the experiment was not sufficient to determine the exact angle, which might be either 45°, as for the alkali-metal (A)-doped polymer AC₆₀ [46], or close to 30°, as suggested by theoretical calculations [63].

As shown in Fig. 6, an orthorhombic structure is obtained over a very wide range of pressure and temperature. However, Agafonov et al. [64] pointed out that X-ray diffraction studies on all material polymerized under “low-pressure” conditions (1.2 GPa, 570 K for Moret et al. [62], 1.5 GPa, 723 K for Agafonov et al.) show slightly different lattice proportions (a=0.91 nm, c=1.47 nm) than material polymerized at lower temperatures (573 K) and very high pressures (5–8 GPa) [7, 57, 64] (a=0.93 nm, c=1.42 nm), although both types of polymers have been identified as having orthorhombic structures. They suggested the possibility that there might exist two different orthorhombic phases. One of these would be the structure described above, which is formed at “low” pressures (the O’ phase, in their terminology), while the other is formed at higher pressures (the O phase). This opens the possibility that the two phases have different rotational angles of the chains, such that the symmetry assignment Immm by Núñez-Regueiro et al. [57] might actually be correct. Support for such a model has been found in resistance studies on nominal orthorhombic C₆₀ polymers. Although optical [65] and electrical [66] studies agree that the band gap of the low-pressure orthorhombic (O’) polymer is smaller than that of molecular (“pristine”) C₆₀.
Polymeric Fullerene Phases Formed Under Pressure

**Fig. 9a–c** Projection along the chains of the structure of the orthorhombic C\textsubscript{60} polymer. *Thick lines* indicate the location of hypothetical interchain bonds to form the tetragonal phase. a Unit cell for a rotational angle of 45°; the central molecule is centered at a/2 and rotated −45°. b Rotational angle 0. c Rotational angle 29°. Reprinted with permission from: R Moret, P Launois, P-A Persson, and B Sundqvist, “First X-ray diffraction analysis of pressure-polymerized C\textsubscript{60} single crystals”, Europhys. Lett. vol. 40 (1997) 55–60 [62]. Copyright © 1997 EDP Sciences

Resistance measurements on materials polymerized at 5–8 GPa (possibly O polymer) indicated *larger* band gaps than for pristine C\textsubscript{60} [66, 67]. In fact, different rotational angles of the chains in linear-chain fullerene polymers also correlate well with differences in electronic band structures in the alkali-metal-doped polymers KC\textsubscript{60} and RbC\textsubscript{60} [68]. KC\textsubscript{60} has the same Pmnn symmetry as the C\textsubscript{60} structure found by Moret et al., with chains forming an angle of 45° to the lattice, and is a metal at room temperature. In RbC\textsubscript{60} all bond planes are parallel, although they do not lie in the same plane as the lattice vectors, and the material is a small-gap semiconductor.

Although the discussion above might indicate that the polymeric structures found under high pressure are always well defined, almost all real material produced at low pressures and temperatures are, in fact, very strongly disordered, and powder samples can often be indexed as either fcc (with a reduced lattice parameter), orthorhombic, or as mixtures of orthorhombic, tetragonal, and rhombohedral structures [7, 58, 59, 69, 70]. Spectroscopic studies also show that many samples contain a high concentration of dimers, C\textsubscript{120}. A glance at either of Figs. 2, 6, or 8 shows that most such materials are produced from fcc C\textsubscript{60}, in which the molecules are rotating in a quasi-free manner. The initial stages of polymerization, involving the formation of dimers and short oligomers, thus occur in random directions since they rely on molecular rotation to bring reactive C=\text{C} bonds on neighboring molecules into close enough contact in the same way as during photopolymerization. Once oligomer “seeds” have been formed, each can
grow into an ordered crystallite or domain, but if the probability of forming such seeds is high and the growth slow, a very disordered network will be formed. Wågberg et al. [71] showed that the structure obtained depended not only on the reaction time and the temperature–pressure coordinates, but also on the pressure–temperature history of the sample. Increasing the pressure to 1 GPa before heating to 577 K for 3 h resulted in a material with a significantly higher fraction of dimers compared to the structure of a sample first heated to 578 K before being pressurized to 1 GPa and treated for the same time. These results could be explained in terms of the reaction kinetics discussed above.

Dimers are always formed as a first step in any polymerization process, and the observation of high concentrations of dimers C_{120} after relatively short reaction times has sometimes been interpreted in terms of the existence of a pure dimer phase. Extensive theoretical calculations of the possible structures of such a phase have also been carried out [72]. However, it is now generally accepted that after a sufficiently long time the final product will always be longer molecular chains [59, 73]. This is shown clearly by the Raman spectra in Fig. 10, measured as a function of reaction time at 1.1 GPa and 530–570 K [59]. Starting from pristine C_{60}, high-pressure treatment initially results in the formation of dimers which, with time, grow or link up to form chains. After 5 h, the line for molecular C_{60} at 1469 cm^{-1} has disappeared, the dimer line at 1464 cm^{-1} has dropped significantly from its peak value at 0.5 h, and the polymer line at 1458 cm^{-1} domi-

![Fig. 10](image)

Fig. 10  Ex situ Raman spectra near the A_{g}(2) mode of C_{60}, measured as a function of reaction time. Characteristic lines for pristine material (1469 cm^{-1}), dimers (1464 cm^{-1}), and chains (1459 cm^{-1}) have been fitted to the spectra to show the structural evolution with time. Reprinted with permission from: P-A Persson, U Edlund, P Jacobsson, D Johnels, A Soldatov, and B Sundqvist, “NMR and Raman characterization of pressure-polymerized C_{60}”, Chem. Phys. Lett. vol. 258 (1996) 540–46 [59]. Copyright © 1996 Elsevier Science BV
nates. Because the growth of dimers is relatively slow at low temperatures it has also been possible to carry out ex situ studies of the kinetics of dimer formation under pressure, and Davydov et al. [74] have shown that the activation energy for the formation of the dimer is approximately 135 kJ mol\(^{-1}\). However, their measurements straddle the fcc–sc phase line, and an alternative analysis gives slightly different activation energies in the two original phases [74].

The disordered dimer-and-chain phase is in many ways similar to photopolymerized C\(_{60}\), and Wågberg et al. [53] have carried out direct comparative studies by polymerizing identical thin films both under pressure and by irradiation by an Ar\(^+\) ion laser (514 nm wavelength). In the initial stages of polymerization, as deduced from the shift of the \(A_g(2)\) Raman mode, the Raman spectra are virtually identical. With increasing polymer fraction, however, the Raman spectra of the photopolymerized samples showed a greater complexity, indicating that they were more disordered. Photopolymerized films also contained a greater concentration of dimers. Both effects can be interpreted as showing that the photopolymerization process is inherently more random. However, the application of pressure might also deform the substrate, adding a shear stress that might help define a polymerization direction for chains to give a better structural order.

At pressures above the rotational transition there is no molecular rotation, and it might be assumed that the polymerization would be inhibited, as observed in the sc phase below 260 K at atmospheric pressure. In fact, polymerization by heating to above 350 K at 3–8 GPa often results in the formation of well-ordered orthorhombic polymers [57, 75], and near the phase line the polymerization rate is often much higher in the sc phase than in the fcc phase at the same temperature [71]. As pointed out by Marques et al. [75], the dominant factors contributing to these features are the lattice compression and the orientational structure. In this pressure range the molecules are initially H oriented (see Fig. 2) when the polymerization occurs. Also, because a reactive C=C bond on each molecule is then oriented toward the center of a hexagon, with three other C=C bonds on its circumference, on its neighbor, and the intermolecular distance is diminished with increasing pressure, a small amplitude thermal librational motion might be sufficient to enable polymerization. Above 3 GPa solid pressure-transmitting media are usually used, and the resulting uniaxial pressure component would also help in defining an initial polymerization direction.

The extrapolated phase boundary between the fcc and sc phases of molecular C\(_{60}\) should thus separate areas with different polymerization mechanisms. As discussed above, Agafonov et al. [64] suggested that at least two different orthorhombic structures might exist, and the difference in structure may, in principle, be correlated with the orientational state of the original molecular C\(_{60}\). The fcc–sc phase boundary might thus also be the approximate boundary between a range at high temperature and low pressure where disordered polymers form, and an area at higher pressures where better ordered orthorhombic polymers are obtained. However, because too little information is yet available this remains a speculation, and the pressure–temperature area indicating the formation of an orthorhombic phase in the reaction diagram in Fig. 6 has thus not been subdivided.
3.2.1.2
Two-Dimensional Structures

When C\textsubscript{60} is treated at 700 K and above, at pressures in the range 1.5–9 GPa, a larger number of intermolecular bonds form and the two-dimensional (layered) phases shown in Fig. 7 are created. The presence of a rhombohedral structure with completely polymerized close-packed planes was observed already in the pioneering experiments of Iwasa et al. [7] and Núñez-Regueiro et al. [57]. The tetragonal phase was observed as a minority or majority phase in many experiments, but usually at relatively low pressures below 4 GPa [75, 76]. The experimental data of Marques et al. [75] showed a very strong correlation between the original rotational state of the material and the appearance of a tetragonal phase. An extrapolation of the sc–fcc phase line to high pressures showed that, to within a reasonable experimental error, the tetragonal phase in their experiments always appeared in samples polymerized from the fcc phase, with quasi-free molecular rotation, and never in samples polymerized from the sc phase with frozen rotation. (A similar comparison made by Marques et al. gave a somewhat different result since they used early, now obsolete, data for the phase line.) Other studies, however, have shown that the tetragonal phase can be produced together with the rhombohedral phase also well into the region where the C\textsubscript{60} should initially have the sc structure [76, 77]; in particular, Wood et al. [77] find a lamellar structure containing a high fraction of tetragonal phase even after treatment at 9 GPa and 773 K.

The tetragonal phase remained relatively unexplored until Davydov et al. [78] showed that it could be prepared in more or less pure, ordered form by simply heating molecular C\textsubscript{60} to the reaction temperature before increasing the pressure to the desired value. In this way, it was possible to reach the reaction pressure and temperature without first passing through any pressure–temperature range where some other polymeric structure is preferred. However, Davydov et al. also report that orthorhombic and rhombohedral polymers transform into the tetragonal structure if annealed for a sufficiently long time near 870 K and 2.2 GPa, and we have confirmed that the kinetics for the formation of the tetragonal structure are practically identical whether the starting material is molecular C\textsubscript{60} or orthorhombic polymer [79]. Calculations also suggest that the tetragonal structure is the most stable of the low-dimensional polymeric structures of C\textsubscript{60} [80].

The structures of the two-dimensional polymers have been determined by several groups. For the tetragonal phase, Núñez-Regueiro et al. [57] suggested a simple stacking sequence in which each consecutive layer was just translationally offset by half the in-plane lattice vectors, giving an Immm symmetry. Davydov et al. [78] had access to almost phase-pure samples, and suggested that the true structure was somewhat more complicated. Their X-ray diffraction data were in better agreement with a structure with an additional 90° in-plane rotation of each consecutive layer [81], such that the chains of “horizontal” intermolecular bonds (see Fig. 7) run in orthogonal directions in neighboring layers. This structure, with the symmetry P\textsubscript{4}2\textsubscript{2}2\textsubscript{m}mc, was also shown by theoretical calculations to be slightly more stable (4 kJ/mol) [81].

Again, detailed structural studies have been carried out on polymerized single crystals. Moret et al. [82] polymerized crystals under hydrostatic conditions
in silicone oil. Because the oil used (Dow Corning DC 200) deteriorates rapidly by polymerization and pyrolysis just above 700 K, the crystals were treated at 2.0 GPa and 700±10 K for 4 h. Although the tetragonal phase is usually reported to be produced only as a minority phase at such low temperatures when using solid (nonhydrostatic) pressure media, the crystals were found to be fully polymerized into the tetragonal phase and even to contain small amounts of the rhombohedral phase. Raman spectroscopy also indicated the presence of a rather high fraction of C_{60} dimers. Again, X-ray diffraction results indicated the existence of orientational domains (variants), but for the tetragonal phase there are only three possible equivalent directions, compared to 12 for the orthorhombic structure [62], making the analysis somewhat simpler. The diffraction studies indicated that the structure was indeed tetragonal with lattice parameters a=0.902 nm and c=1.493 nm, and also verified the P4_{3}32/mmc symmetry suggested by Davydov et al. [78, 81]. No indications of dimers or a dimer lattice were found, indicating that these probably formed a disordered surface layer only. Somewhat surprisingly, the lattice parameters found are smaller than the values obtained from analyses of powder samples treated at higher pressures and temperatures: tetragonal powder samples produced at 2.2 [78] and 2.5 [76] GPa, both at 873 K, and at 4 GPa and 973 K [57], show lattice parameters a of 0.910, 0.907, and 0.909 nm and c of 1.504, 1.511, and 1.495 nm, respectively.

Very recently, another single crystal study has been carried out by Chen and Yamanaka [83]. Their crystals were polymerized under somewhat more harsh conditions for 2 h at 2.5 GPa and 773 K, with the crystals embedded in compacted hexagonal BN powder (h-BN) which can be considered a “quasi-hydrostatic” environment. Attempts to synthesize the tetragonal phase using the Davydov and Moret p–T trajectory (first heating, then pressure) failed (all 80 crystals tested were too deformed to be used), but some crystals heated at the reaction pressure survived intact. Three crystals were analyzed in detail by X-ray diffraction. While the general in-plane topology was the same as in previous studies on the tetragonal phase, Chen and Yamanaka found that all crystals are actually orthorhombic (although “quasi-tetragonal”) with symmetry group Immm (all layers oriented identically) and lattice parameters 0.9026, 0.9083, and 1.5077 nm, close to those obtained in other studies. Powder X-ray diffraction studies on crushed polymer synthesized by the Davydov method also indicated an Immm symmetry. There is at present no good explanation for the large differences between these results and those of Davydov et al. and Moret et al. It has been suggested [83] that the different preparation methods might be the cause, but further structural studies are clearly needed.

The structure of the rhombohedral phase was studied very early, by both experiments [7, 57] and calculations [57, 84, 85]. The lattice was shown to have an ABCABC stacking with R3m symmetry, as might be expected when formed from the (111) plane in a fcc lattice (Fig. 7). However, the details of the structure were questioned by Davydov et al. [81], who suggested that a different stacking arrangement would have a significantly lower total energy. Again, the rhombohedral structure has very recently been restudied in detail on polymerized single crystals. The nominally tetrahedral crystals synthesized by Moret et al. [82] at 2 GPa and 700 K also contained a fraction of rhombohedral material, large
enough to identify the stacking sequence. Chen et al. [86] synthesized rhombohedral C$_{60}$ by treating small crystals at 5 GPa and 773 K for 1 h, again using a solid pressure-transmitting medium (h-BN), and found several single-domain crystals that could be studied in great detail. Both groups agree that the alternative stacking model of Davydov et al. is in better agreement with experiment than the structure originally suggested by Núñez-Regueiro et al. [57], and Chen et al. [86] give detailed information about the structure, including atomic coordinates and bond lengths. The difference between the two structures discussed is superficially quite small within each plane, as shown in Fig. 11, where the pentagonal faces have been shaded to show the differences. Again, we point out that the planes of the intermolecular bonds in the three trigonal directions make an angle of ±20.2° [86] with the polymer plane. However, in the structure of Núñez-Regueiro et al., carbon-atom pentagons on nearest neighbors in adjacent layers face each other, while in the structure identified by Moret et al. and Chen et al. hexagons face each other. This fact agrees well with the observation that the rhombohedral structure is the majority phase formed on polymerization from simple cubic, H orientationally ordered C$_{60}$ at high temperature [75]. Only a small molecular rotation is thus needed to form the polymer.

Because a rather high pressure is needed, most two-dimensional C$_{60}$ materials are produced under nonhydrostatic conditions using solid pressure media. This gives rise to directional effects on the structure, such that macroscopic samples taken out of the pressure cell often have a layered morphology and a strong preferential lattice orientation, giving rise to a prominent anisotropy in many macroscopic properties [87, 88]. The anisotropy can also be observed in studies of the microscopic structure, either as a preferred lattice orientation [23, 24, 28] or, more interestingly, as an anisotropy in the lattice parameters [22, 25, 27]. In the latter case, Debye–Scherrer ellipses are observed instead of circles in diffraction studies. Such features were first observed only in polymeric C$_{60}$ produced under extreme conditions [22, 25], but very recent studies in the range 2–6 GPa,
where two-dimensional polymers are formed, show similar features [27]. Marques et al. studied the Debye–Scherrer anisotropy as a function of time and pressure–temperature trajectory, and concluded that polymerization proceeds preferentially along the direction of the uniaxial pressure component [27]. The gradual formation of two-dimensional polymers could be followed through the evolution of the diffraction pattern from circles (unmodified C\textsubscript{60}), over ellipses (molecular C\textsubscript{60}, high anisotropic pressure), and until the ellipses collapsed into patterns typical for textured materials. Interestingly, samples treated using the method of Davydov et al. [78] did not become fully polymerized at 873 K, even at several GPa, although those heated to the same final conditions at full applied pressure did. This result, which differs from other recent results [78, 82, 83], is claimed to arise from the lower pressure anisotropy in the sample when compressed at high temperature.

### 3.2.1.3 In Situ Studies of Polymerization

The discussion up to this point has only treated polymeric materials studied ex situ, usually after being quenched back to room temperature and removed from the high-pressure vessel. However, it is of obvious interest to find which of the low-dimensional structures discussed are true quasi-equilibrium phases, stable under particular pressure–temperature conditions. A small number of in situ studies have recently been carried out under elevated pressure and temperature to answer this question, both by X-ray diffraction [17, 89] and Raman spectroscopy [19, 25].

The first to carry out systematic in situ studies under high pressure and temperature were Bennington et al. [17], who made X-ray diffraction studies between 300 and 1100 K at 2.6 and 5.7 GPa. The results were in reasonable agreement with the reaction diagram in Fig. 6, if we take into account that disordered, quasi-cubic diffraction diagrams are often found [7, 59] for the orthorhombic phase. At 2.6 GPa such a cubic lattice was observed until above 700 K, where a tetragonal phase appears and grows until it collapses at 1130 K. Similarly, at 5.7 GPa the cubic phase was replaced by a rhombohedral structure above 650 K. Wood et al. [89], on the other hand, made high-pressure, isothermal X-ray diffraction studies at 800 K and found a gradual conversion of the tetragonal phase, created near 1 GPa, into the rhombohedral phase in the range up to 8 GPa.

Raman spectroscopy has also recently been used for in situ studies by Talyzin et al. [19], using a diamond anvil cell setup in a temperature-controlled oven. In their experiments, heating resulted in a rapid, reversible pressure decrease, and the measurements were therefore carried out along a diagonal in the reaction diagram of Fig. 6. Experiments started near 5.5 GPa at room temperature, where a certain fraction of dimers or short chains were observed, as in many other experiments [6, 13, 14]. Heating to 780 K brought the pressure down to an estimated 1.5 GPa. During this heating run, the measurements indicated a continuously increasing degree of polymerization until the temperature reached 670 K, but after this a final depolymerization into molecular C\textsubscript{60} was found at the highest temperature. Although the analysis was complicated by the temperature and pressure...
dependence of the Raman lines, again the general results agree well with the map in Fig. 6. Both orthorhombic and tetragonal phases appear on heating near 450 K (at about 3.5 GPa), and near 670 K (2.3 GPa) there is also a significant amount of the rhombohedral phase present. The depolymerization observed indicates that heating has brought the pressure down below the equilibrium line between polymer and molecular solid [58] (Figs. 6 and 8). Using the observed slope of 390 K GPa\(^{-1}\) for this phase line we find that the pressure at 780 K was actually below 1.25 GPa. (This slope has been verified by two other groups, who both found that no polymerization occurs at 1.5 GPa and 900 K [90, 91].) On cooling, the pressure increased again and polymers were re-formed. In this run, linear chains and tetragonal planes dominate, in agreement with what might be expected from the discussion above and in previous sections. However, from data obtained at low pressures it is suggested that, close to the fcc-polymer phase line mapped by Bashkin et al. (Fig. 8), a narrow region might exist in which the orthorhombic rather than the tetragonal phase is stable. Ex situ X-ray diffraction studies on samples recovered after the high-pressure experiment verified the Raman identification of the structures observed, and also showed a strong anisotropy in the lattice orientation, correlated with the uniaxial component of the pressure.

Talyzin et al. also carried out similar experiments, starting at 10, 14, and 18 GPa at 290 K and heating to about 800 K [25]. Again, during each run the pressure dropped by about 5 GPa. All experiments gave similar results. Starting from a mixture of molecular \(C_{60}\) and dimers, polymeric structures (both chains and planes) appeared at 470 K. At 570 K both the tetragonal and rhombohedral phases are present, and at higher temperatures the rhombohedral phase dominates. On cooling, no significant further changes are observed. Ex situ X-ray studies showed the presence of the rhombohedral phase only, but the Raman spectra also showed lines from the tetragonal and orthorhombic phases, evidently present as minor impurity phases. The results obtained in the 10-GPa runs thus also agree well with the map in Fig. 6. Surprisingly, Talyzin et al. found very similar results also starting at 14 and 18 GPa, except that the conversion into the rhombohedral phase occurred at a higher temperature, and we return to this result below.

To summarize, the results of recent in situ studies up to 10 GPa under semi-equilibrium conditions thus verify all the major features of the “reaction map” in Fig. 6. This part of the pressure–temperature reaction diagram of \(C_{60}\) can therefore be considered to be well understood.

### 3.2.1.4 Physical Properties of Low-Dimensional Polymers

The physical properties of the low-dimensional phases have already been well studied, and early results have been reviewed elsewhere [12–14]. This section will therefore concentrate on some key properties and recent results.

The basic difference between molecular and polymeric \(C_{60}\) is the presence of covalent intermolecular bonds in the latter. The existence of such bonds has most clearly been shown by \(^{13}\)C nuclear magnetic resonance (NMR) studies on orthorhombic [59, 92], tetragonal [93], and rhombohedral \(C_{60}\) [60, 92]. NMR gives
very different frequency shifts for sp² and sp³ hybridized carbon, allowing a clear identification of intra- and intermolecular bonds. Although long relaxation times make experiments very time-consuming, the relative numbers of sp² and sp³ hybridized atoms in each phase have been shown to agree with those expected from the structural models, and the sp² peak can be decomposed into lines corresponding to the number of unique carbon atom environments [60, 93].

All polymers created under pressure break down to molecular C₆₀ if annealed at high temperature near atmospheric pressure. Dimers break down near 420 K [47, 94], but the orthorhombic structure is stable to about 500 K and the tetragonal [94] and rhombohedral phases [95] to above 550 K. Since breakdown is a thermal process, this thermal “stability limit” depends on the timescale, and a better stability indicator is the activation energy $E_a$ needed to break down the sp³ bonds. Interestingly, different methods give different values for this quantity. Nagel et al. [94] find that for dimers $E_a=1.75$ eV, while for orthorhombic and tetragonal C₆₀ $E_a=1.9$ eV, in reasonable agreement with theoretical estimates [80, 85, 96]. Optical studies give much lower values, probably because optical excitation of a C₆₀ molecule in a polymeric structure significantly lowers the threshold for thermal breakdown [65, 97, 98]. We note also that the values observed are

Fig. 12  Raman spectra for pristine, orthorhombic, tetragonal, and rhombohedral C₆₀ using a 514-nm Ar⁺-ion laser for excitation. The rhombohedral sample was produced from high-purity powder and all others were originally single crystalline material. Spectra collected by Dr. Thomas Wågberg, Umeå University, Sweden
much lower than the value of 3.6 eV found for the sp³ bonds in diamond because of the strained bond angles, which are close to 90°.

Polymerization changes both the microscopic and the macroscopic properties of the material. The intramolecular lattice vibrations change relatively little, but because the symmetry is lowered a large number of previously forbidden lines appear in the Raman and IR spectra. This was observed already in pioneering experiments on polymeric C_{60} [6–8], and a very large number of spectroscopic studies have been carried out on polymeric materials with different structures.
and various degrees of purity. Data for high-purity materials have been collected in Figs. 12, 13, and 14. Even a cursory glance at the curves in these figures shows that spectra for different structures are very different, and that typical “fingerprints” for the different phases can easily be found. Spectroscopy is thus a rapid and powerful tool to obtain local information about the structures created. Both IR and Raman spectra have been analyzed in detail elsewhere [99, 100], and only two important points are mentioned here. First, polymers are usually identified from the shift of the high-intensity Raman $A_g(2)$ mode, which at room temperature falls at 1469 cm$^{-1}$. The formation of intermolecular bonds shifts the electron density away from the remaining double bonds, which become weaker. This causes a negative shift in the $A_g(2)$ mode to approximately 1464 cm$^{-1}$ in dimers, 1459 cm$^{-1}$ in linear chains, 1447 cm$^{-1}$ in the tetragonal structure, and 1407 cm$^{-1}$ in the rhombohedral phase. Second, the presence of sp$^3$ intermolecular bonds also causes new bands to appear in the range 900–1000 cm$^{-1}$.

The intermolecular vibrations are very strongly affected by polymerization, since weak van der Waals interactions are replaced by covalent bonds. In the Raman spectra, new intermolecular modes appear at 97 cm$^{-1}$ in dimers [71, 101] and at 118 cm$^{-1}$ in molecular chains [8, 71], and neutron scattering shows a significant upward shift in the density of vibrational states [102–104]. A simple argument shows that for each direction of polymerization, one third of the original low-fre-

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**Fig. 14** Far-infrared transmittance spectra for rhombohedral (R) and orthorhombic (O) $C_{60}$ polymers, and for $C_{60}$ dimers, measured near 20 K. Curves are offset for clarity. Reprinted with permission from: VC Long, JL Musfeldt, K Kamarás, GB Adams, JB Page, Y Iwasa, and WE Mayo, “Far-infrared vibrational properties of high-pressure high-temperature $C_{60}$ polymers and the $C_{60}$ dimer”, Phys. Rev. B vol. 61 (2000) 13191–201 [100]. Copyright © 2000 The American Physical Society
frequency “Debye” acoustic modes are pushed up to significantly higher energies. As shown in Fig. 15, this has large effects on the low-temperature specific heat of C\textsubscript{60} which is dominated by low-frequency vibrational and librational modes [105, 106]. Other thermodynamic properties are also affected. The thermal conductivity should in principle increase strongly, but this seems to be compensated for by an increased disorder [61], and along the polymerization directions the thermal expansion decreases from values similar to those along the axis in graphite to the near-zero values observed in diamond [94]. The compressibility should also decrease strongly in the directions of polymerization, such that the bulk modulus B should increase by approximate factors of 1.5 in the orthorhombic phase and 3 in the tetragonal one. A recent study finds the bulk modulus of tetragonal C\textsubscript{60} to be B(0)=34.8 GPa [107], a little more than three times higher than the recommended value for molecular C\textsubscript{60} given above. Similar values were found by Bashkin et al. [58] for low-pressure polymerized disordered material.

The electronic properties are also modified by polymerization. Experimentally, the band gap decreases to less than 1.2 eV in the low-pressure orthorhombic phase [65], and experiments [66, 88, 108] and calculations [80, 109–111] agree that the band gap should decrease with an increasing number of intermolecular bonds. (We note the possible exception of the “high-pressure polymerized” orthorhombic phase, as discussed above.) Calculations [85, 111] show that the rhombohedral phase should have a more three-dimensional band structure than the orthorhombic phase but still be a semiconductor. However, recent measurements by Makarova et al. [88] showed that oriented samples of the rhombohedral phase had an extremely large electrical anisotropy, larger than that of single-crys-

![Fig. 15](image)

**Fig. 15** Low-temperature molar specific heat of tetragonal (filled triangles), orthorhombic (dots), and depolymerized C\textsubscript{60} (open symbols), plotted as C\textsubscript{p}/T\textsuperscript{3}. Reprinted with permission from: A Inaba, T Matsuo, Å Fransson, and B Sundqvist, “Lattice vibrations and thermodynamic stability of polymerized C\textsubscript{60} deduced from heat capacities”, J. Chem. Phys. vol. 110 (1999) 12226–32 [105]. Copyright © 1999 American Institute of Physics
tal graphite. The on-axis resistivity was very high and decreased with increasing temperature, but the conductivity mechanism could not be determined. The resistivity in the polymerized plane showed a metallic behavior at room temperature, but below a certain temperature which depended on treatment conditions, a logarithmic increase in resistivity with decreasing temperature was found. This effect was tentatively ascribed to weak localization of carriers. The metallic behavior could possibly arise because of a self-doping effect. Polymerization into the rhombohedral phase at high temperature is a rapid process, and some C\textsubscript{60} molecules might be incorporated into the structure in the wrong orientation with bonds forming along boundaries between hexagons and pentagons. Recent band structure calculations show that such lattice defects may give rise to a metallic behavior [112].

Disordered low-dimensional C\textsubscript{60} polymers also show interesting magnetic properties. In particular, Makarova et al. [16] reported that rhombohedral C\textsubscript{60} polymerized at high temperatures near 6 GPa showed signs of weak ferromagnetism (nonlinear susceptibility and magnetic hysteresis loops, as shown in Fig. 16) at temperatures well exceeding room temperature. This has been verified

Fig. 16 Magnetization loops at 10 and 380 K, and magnetization versus temperature, for a sample of rhombohedral C\textsubscript{60} treated at 6 GPa. Figure courtesy of Dr. Tatiana L. Makarova, Umeå University, Sweden, and the Ioffe Institute, St. Petersburg, Russia
by other groups, working in other ranges of pressure [113, 114]. Such signatures of ferromagnetism, at and above room temperature, have also been found in phototransformed C$_{60}$ [115], in metal–fullerene compounds [116], in hydrofullerides H$_x$C$_{60}$ [117], and even in pure graphite [118]. A plot of treatment coordinates versus temperature and pressure (Fig. 17) shows that ferromagnetism in pure C$_{60}$ only appears in a temperature range just below where the molecules break down. Although ferromagnetism in carbon is not well understood, in the fullerenes there seems to be a strong correlation with molecular defects. Calculations by Andriotis et al. [119] show that such defects may indeed lead to magnetic signals in C$_{60}$ polymers, primarily in linear-chain materials and rhombohedral materials. This agrees well with the experimental observations of ferromagnetism in phototransformed and pressure-polymerized C$_{60}$. Material treated near 2.5 GPa contains mainly the tetragonal phase, and the very weak magnetic signals obtained in this material may well arise from a rhombohedral minority phase (T.L. Makarova, private communication).

3.2.2
Three-Dimensional Polymers

Above 9 GPa the C$_{60}$ molecules are pressed very close together and an increase in temperature leads to very rapid polymerization. Most samples therefore become strongly disordered and there is little consensus about the structures observed. Some of the structures identified may be quasi-equilibrium phases, in analogy with the low-dimensional polymers already discussed, while others may be intermediate transitory states. Both amorphous and crystalline states have
been observed in the very large number of studies that have been published, and many of the materials produced have extreme elastic and hardness properties. In spite of the many interesting discoveries made in this pressure range this section will be kept short and focused on some recent results of particular interest, both because of space limitations and because an extensive overview has recently been given by Blank et al. [12].

3.2.2.1
Ex Situ Studies of 3D Polymerization

As discussed elsewhere [12], several groups have heated C₆₀ to high temperatures for one or several minutes under high pressures, then quenched the samples back to 290 K before decreasing the pressure to zero. In the range 9–15 GPa, a very similar evolution is found with increasing treatment temperature, although at higher pressures, lower temperatures provoked the same structural changes. Many samples contain dimers or short chains already at room temperature (see above), and heating results in a rapid volume decrease when intermolecular bonds are formed. Because this occurs in random directions, structural studies usually indicate a fcc structure up to temperatures of several hundred K, but below 11 GPa linear chains often form before this cubic phase takes over. Although no change is observed in the lattice structure, the macroscopic hardness increases rapidly and “hard fcc” materials easily cut cubic BN with a hardness of 9.5 on the Mohs scale (only exceeded by that of diamond). The increase in hardness is correlated with the lattice constant and occurs near a lattice constant of 1.36 nm. At high temperature, disorder leads to broadening and intensity loss in the diffraction peaks, but peaks indicating a fcc lattice with very strained molecules have been detected with lattice parameters even below 1.2 nm in a sample treated at 13 GPa and 900 K [120]. Under such extreme conditions new features appear in the XRD diagrams, possibly signifying partial molecular collapse or formation of small local clusters of carbon atoms.

Above 10 GPa most samples contain multiple “phases”. Body-centered and monoclinic structures have been identified, usually distorted, and disorder, distortions, and density increase with temperature. Although Raman spectra become increasingly featureless with increasing severity of treatment conditions, distinct lines near 500, 710, and 770 cm⁻¹ could be correlated with the A₆(1), H₆(3), and H₆(4) modes of C₆₀ and showed that at least some molecules are still intact under these extreme conditions.

Attempts have recently been made to investigate the lattice structures appearing in this region in more detail using synchrotron radiation [22, 121, 122]. Very strong effects due to anisotropic pressure were found, with elliptical Debye–Scherrer patterns indicating direction-dependent lattice parameters. The formation of three-dimensional fullerene structures with a very high concentration of intermolecular bonds evidently had frozen in the uniaxial lattice compression due to pressure anisotropy, allowing this to be observed even under ambient conditions after the experiments [22]. From simulations of some possible structures it was concluded that the most probable structure of the three-dimensional phases produced near 13 GPa at 670–820 K (“bcc” range in Fig. 6)
is a body-centered orthorhombic Immm structure with an intermolecular distance of only 0.88 nm [121, 122]. The authors suggest that the synthesis of this structure starts with formation of chains by “normal” (2+2) cycloaddition, followed by two-dimensional polymerization through a mechanism resulting in common four-sided rings between molecules. At higher temperatures, further bonds may form between layers by a (3+3) cycloaddition reaction resulting in a three-dimensional polymer. An alternative, zeolite-like structure may be formed at slightly lower pressures [122]. The observed X-ray diffraction results agree well with the structures suggested [121, 122].

These three-dimensional fullerenes show interesting mechanical and thermal properties, although there is poor agreement between results from different groups. Although a bulk modulus exceeding that of diamond has been reported [12, 121–123], other experimental and theoretical [124] work indicate somewhat lower values.

Above 900 K, a very hard amorphous phase with a density of 2.4–2.8 g cm\(^{-3}\) is obtained [12, 14]. X-ray diffraction shows a 002 halo giving an interplanar distance of 3.0–3.3 Å, depending on treatment conditions. This structure is probably based on intact C\(_{60}\) molecules, linked into a disordered structure with nm-size crystallites. Many properties are similar to those of amorphous graphite- or diamond-like films, but closer analysis shows the uniqueness of this phase [12]. Although an AFM study [125] found intermolecular distances of only 6.5–7.7 Å, indicating partial molecular breakdown, mass spectrometry [126] and Raman data show the building blocks to be intact C\(_{60}\) units. Several structural models have been suggested [12], including a “barrelene” model [127] where the C\(_{60}\) molecules transform into an elongated shape with dimensions in good agreement with the AFM results.

Finally, above about 20 GPa polymerization may also occur at room temperature, as observed in many early works [12–14, 41, 128–131]. Although most authors find disordered phases above this transition, crystalline phases may also be found as shown in the next section.

3.2.2.2 In Situ Studies of 3D Polymerization

Most three-dimensional polymer samples have been produced by short-time heating under high pressure, and quasi-equilibrium in situ studies over longer times are therefore of obvious interest. A small number of such studies have indeed been carried out recently. Bennington et al. [17] made an X-ray study at 12 GPa and found a basically cubic structure at all temperatures up to about 1000 K, where all peaks disappeared as a disordered phase appeared. Similar results were found by Horikawa et al. [18] in a time-resolved study at 12.5 and 14.3 GPa, following the evolution of the structure over up to 3 h at each temperature. On continuous heating the lattice was stable to about 900 K, while at constant temperature a gradual amorphization occurred over a time scale of about 1 h near 700 K at both pressures. During this time the lattice parameters decreased continuously with time. Talyzin et al. have carried out both Raman [25, 132, 133] and X-ray [134] studies under in situ conditions. The X-ray stud-
ies were made in the range 13–18 GPa and up to 830 K, and each heating run had a duration of up to 3 h. The 18-GPa sample showed strong anisotropic effects, with elliptical Debye–Scherrer traces, and transformed from a cubic phase into an amorphous phase above 550 K. At lower pressures the structures obtained on heating could be indexed in terms of a rhombohedral structure with a reduced volume compared to the two-dimensional rhombohedral phase, and the authors identify this as a three-dimensionally polymerized material. Earlier Raman studies in situ at 10–18 GPa [25] had only detected the presence of the well-known two-dimensional polymers, possibly because the three-dimensional phases have a practically featureless Raman spectrum.

The “amorphous” phase appearing above 20 GPa at room temperature (see above) has also recently been studied by X-ray diffraction [135] and Raman scattering [132, 133]. Serebryanaya et al. [135] identify the structure as a three-dimensionally polymerized Immm orthorhombic lattice, but find that compression above 40 GPa gives a truly amorphous structure. In contrast to the orthorhombic three-dimensional polymer structure discussed in the last section, the best fit here is found for (2+2) cycloaddition in two directions, with (3+3) cycloaddition in the third, and thus some relationship to the tetragonal phase. From the in situ X-ray data a bulk modulus of 530 GPa is deduced, about 20% higher than for diamond. Talyzin et al. [132, 133] find that this phase depolymerizes on decompression into linear polymer chains, unless the sample is heated to above 575 K under pressure. A strong interaction with the diamond substrate is also noted, such that only films with a thickness of several hundred nm are able to polymerize fully [132]. Hardness tests were also carried out on the polymerized films, which were found to be almost as hard as diamond and to show an extreme “superelastic” response with a 90% elastic recovery after indentation [133].

Although the actual structures identified differ, it thus seems that both in situ and ex situ studies agree that crystalline three-dimensional polymers are indeed formed at very high pressures on heating of C_{60} to above 300–400 K.

3.2.2.3 Transformations from 2D to 3D Structures

It is obvious from the discussion above that the identification of the three-dimensional lattice structures observed is very difficult due to their disordered nature. A possible way to obtain well-defined three-dimensional polymeric structures would be assembly from well-known one- or two-dimensional precursors. Okada et al. [136] suggested that room temperature compression of the Immm tetragonal structure along the axis would result in the formation of a stable three-dimensional structure near 20 GPa. Calculations predicted a metallic material with a high density of states. Burgos et al. [137] studied compression of both one- and two-dimensional polymers and suggested that three other high-pressure phases, all semiconducting, could possibly be created below 15 GPa. The experiment suggested by Okada et al. was carried out by Meletov et al. [138], who found that the tetragonal material did indeed become amorphous near 20 GPa and that a new phase with a different Raman spectrum appeared above this. This new phase was later shown to be metastable for a short time near atmospheric pres-
sure [139], but its structure could not be determined. The material broke down explosively into molecular fullerene, dimers, and possibly diamond-like carbon, and a large fraction of the molecules are thus intact after the experiment. Direct structural studies in situ have verified the amorphization of the material, but failed to detect any new crystalline structure at higher pressures [107], even after in situ laser heating.

Similar studies have also been carried out on rhombohedral C\(_{60}\), compressed under the same conditions [140]. This phase is marginally less stable and transforms into an amorphous phase near 15 GPa, in reasonable agreement with the prediction of Burgos et al. [137]. Annealing the new phase at atmospheric pressure recovers molecular and dimeric C\(_{60}\), and it is concluded that the high-pressure phase consists of randomly interconnected polymerized close-packed C\(_{60}\) planes.

High temperature usually promotes polymerization, but no effect of heating was found on the formation of three-dimensional phases from tetragonal C\(_{60}\) [107]. Buga et al. [141] tried submitting rhombohedral C\(_{60}\) to a pressure of 13 GPa and temperatures in the range 620–1620 K. After treatment, the structures observed were similar to those observed after treatment of pristine C\(_{60}\) under identical conditions. Below 700 K, an Immm body-centered orthorhombic structure was found and at higher temperatures disordered phases appeared. Differential scanning calorimetry showed that the crystalline material broke up into intact molecules near 550 K, and all samples showed very unusual electrical transport effects.

All these studies show that two-dimensional phases turn into amorphous, probably three-dimensionally polymerized material under conditions very similar to those where pristine, molecular C\(_{60}\) does. Because the end products also seem very similar, questions arise about the relationships between two- and three-dimensional polymers. In particular, do the polymeric phases break down into molecular C\(_{60}\) before three-dimensional polymerization, or are two-dimensional polymers always formed as precursors to three-dimensional polymers?

### 3.2.3 Molecular Breakdown Under Extreme Conditions

The C\(_{60}\) molecules are surprisingly stable, but heating to above 1000 K or compression to above 40 GPa [135], or a combination of similarly extreme conditions, give permanent changes to the material which must be interpreted in terms of molecular breakdown.

Below 10 GPa, heating to near 1000 K leads to the formation of a very disordered, hard black phase first found by Kozlov et al. [142] near 3 GPa. In Fig. 6 these phases are labeled “partially graphitized fullerite”. The material is layered, turbostratic, and graphite-like but strongly cross-linked by sp\(^3\) bonds [143, 144] and not always stable with time. Although the structure may be similar to those of graphite or glassy carbon the material is very much harder than these because of the interplanar bonds, which also gives a mesoscopic corrugation or modulation to the layered structure. Like amorphous carbon and graphite it is a semimetal with an almost temperature-independent resistivity [142]. Its formation [77], structure [77, 144], and acoustic and thermal transport properties [145, 146] have
recently been investigated in some detail. With increasing treatment temperature
the material becomes increasingly softer and more graphite-like, as might be
expected. An interesting observation is that this disordered material may show
orientational effects on the structure, related to the uniaxial pressure applied
during synthesis, in the same way as the crystalline phases discussed above.
This gives rise to an anisotropy in the measured elastic properties of the final
material [26].

At very high pressures, above 12 GPa, and temperatures above 1000 K, a trans-
parent, yellowish, “ultra-hard” material, believed to consist of the remnants of col-
lapsed molecules, is formed. In several cases ultrasonic, scratch, and indentation
studies have shown this material to have a bulk modulus and hardness far ex-
ceeding that of diamond [123, 131, 147], although these reports are by no means
uncontested [124, 148, 149]. The material is extremely disordered and probably
has a high fraction of sp² coordinated bonds, but the structure is unknown. There
are some similarities with amorphous carbon (ta-C), but differences in Raman
spectra and mechanical properties show that the structures differ. The question
of bond types is interesting, since sp² bonds are known to be stronger than sp³
ones. The materials are semiconducting and have Debye temperatures near
1450 K, somewhat lower than that of diamond [150].

Finally, C₆₀ can also break down into diamond [12, 14]. This, however, only
occurs under extreme conditions, above 2000 K at pressures exceeding 10 GPa,
or under shock compression conditions.

3.3
Polymerization of Higher Fullerenes

C₇₀ is the only “heavy” fullerene easily available in significant quantities, and is
therefore the only fullerene besides C₆₀ that has been well studied so far. As men-
tioned above, only the five bonds radiating out from each polar pentagon have a
significant reactivity, and this gives strict topological constraints on the forma-
tion of long-range ordered polymers of C₇₀. It is not only necessary to bring the
molecules sufficiently close together; they must also be correctly oriented. At high
temperatures the molecules rotate quasi-freely and C₇₀ can be polymerized by
radiation just like C₆₀ [151], but the reaction is slower and cluster size is limited
to mainly dimers, C₁₄₀ [56].

Early high-pressure studies on C₇₀ were inconclusive [13, 14]. Of particular
interest is the report by Chandrabhas et al. [152] that intramolecular Raman
modes could be observed up to 12 GPa, but that above 20 GPa the Raman lines
of C₇₀ were replaced by a new line at 1650 cm⁻¹, characteristic of amorphous
carbon. Surprisingly, the amorphization was reversible, and normal Raman sig-
nals were found after decreasing pressure. Although this might indicate the
reversible formation of disordered polymers, Sundar et al. [153] found no signs
of polymers after heating hcp C₇₀ up to 1100 K for up to 6 h at 5 and 7.5 GPa.

Later work [36, 154], however, clearly showed that C₇₀ polymerizes under high-
pressure conditions. Iwasa et al. [154] treated C₇₀ at elevated temperatures for 1 h
at 5 GPa. Characterization by solubility tests, X-ray diffraction, IR spectroscopy,
and UV/visible absorption spectroscopy showed clear signs of polymerization in
both hcp and fcc C\(_{70}\), after treatment at 473–573 K. IR spectroscopy showed many new modes, in good agreement with theoretical calculations, and the material reverted to molecular C\(_{70}\) after annealing near 600 K. Above 670 K disordered graphite-like materials were formed under pressure, indicating that C\(_{70}\) is more sensitive to high-temperature treatment than C\(_{60}\). Although Iwasa et al. were unable to identify the structure, Premila et al. [36] found the high-pressure-treated phase to have a disordered rhombohedral lattice. A much more extensive study was carried out by Blank et al. [155], who mapped the reaction diagram of C\(_{70}\) between 4 and 12.5 GPa in much the same way as for C\(_{60}\) (cf. Fig. 6). Their work indicated that the reaction diagram of C\(_{70}\) shared some general features with that of C\(_{60}\), but contained significantly fewer phases. As shown in Fig. 18, a rhombohedral, two-dimensional R3m polymeric phase is obtained over a wide range of temperature and pressure. At very high temperature and low pressure graphitic phases should be formed, while above 800–1100 K, depending on pressure, various “hard carbons”, amorphous, or cross-linked graphite-like structures similar to those formed in C\(_{60}\) under similar conditions, are observed. At pressures above 9 GPa tetragonal, very hard, three-dimensional polymers are formed. However, all polymerized materials are extremely disordered and structural analysis has also shown other possible structures, such as chains of dimers [156]. As was the case for C\(_{60}\), room-temperature studies also show polymerization to occur at sufficiently high pressures. Chandrabhas et al. [152] found reversible amorphization above 20 GPa, but this was later shown to be irreversible on application of pressures higher than 35 GPa [157]. In situ Raman spectroscopy, X-ray diffraction [158], and resistivity [159] studies have been carried out on this phase, which is amorphous, insulating, and has a hardness which is a significant fraction of that

---

**Fig. 18** “Reaction map” for C\(_{70}\), based on data from Refs. [155, 162, 164, 165], showing the structural phases obtained after short-term treatment under the conditions shown.
of diamond. As a general rule, the properties of polymeric C\textsubscript{70} thus do not differ very much from those of the corresponding phases of C\textsubscript{60} [36, 154, 155, 157–161].

Quite recently, it has been shown that C\textsubscript{70} can also polymerize at much lower pressures. Early thermal conductivity studies on C\textsubscript{70} at 450 K near 1 GPa by Dr. A. Soldatov (private communication) showed an increasing degree of disorder over several days, indicating polymerization. Further experiments showed [162] that both powdered and single-crystal C\textsubscript{70} polymerized if treated in the range 1–2 GPa and 500–600 K for long times, up to 16 h. Figure 19 shows Raman spectra for both pristine C\textsubscript{70} and for two toluene-insoluble materials obtained after treatment at high temperature and high pressure. The latter two spectra show several new features, including low-frequency intermolecular modes near 90 and 105 cm\textsuperscript{-1} for samples treated near 1.1 and 2 GPa, respectively, indicating the formation of dimers at low pressures and longer chains near 2 GPa. Careful studies showed that out of the five possible isomers of C\textsubscript{140} [163], only the almost end-

![Raman spectra for pristine C\textsubscript{70}, C\textsubscript{70} dimers, and orthorhombic C\textsubscript{70} polymer containing zigzag chains.](image)

**Fig. 19 a–c** Raman spectra for a pristine C\textsubscript{70}, b C\textsubscript{70} dimers [164], and c orthorhombic C\textsubscript{70} polymer containing zigzag chains [165]. Reprinted with permission from: A Soldatov, P Nagel, V Pasler, S Lebedkin, C Meingast, G Roth, and B Sundqvist, "Polymeric fullerenes: from C\textsubscript{60} to C\textsubscript{70}”, In: Kuzmany H, Fink J, Mehring M, Roth S (eds) Electronic properties of novel materials – science and technology of molecular nanostructures (CP486, American Institute of Physics, Melville, NY, 1999) pp 12–15 [162]. Copyright © 1999 American Institute of Physics
to-end form with parallel axes was formed in the experiments [164]. As indicated in the phase diagram for C\textsubscript{70} shown in Fig. 3, compression near room temperature causes the axes of neighboring molecules to line up in parallel perpendicular to the close-packed planes, and the uniaxial rotation of the molecules makes dimerization possible between molecules in adjacent layers. Because the reaction is random the final product was a disordered mixture of dimers and unreacted residual C\textsubscript{70}, which could be dissolved in o-dichlorobenzene. An almost pure dimer phase was then extracted by chromatography and studied by NMR, IR, Raman (Fig. 19), optical absorption, and fluorescence spectroscopy, mass spectroscopy [162, 164], and thermal expansion measurements [94, 162].

Although dimers thus easily form during high-pressure treatment of C\textsubscript{70}, it is much more difficult to create larger ordered clusters because of the geometrical constraints mentioned above. When the molecules in solid C\textsubscript{70} line up with their axes in parallel under pressure, the five-fold symmetry of the molecules is incompatible with the three-fold symmetry of the standard fcc lattice in the (111) direction, and no ordered structure can form. However, the ABAB stacking of the hcp lattice might enable the formation of ordered arrays of zigzag chains perpendicular to the close-packed layers. To test this idea, Soldatov et al. [165] annealed single C\textsubscript{70} crystals with a predominantly hcp structure under hydrostatic conditions (in silicone oil) at 2 GPa near 500 K for 11 h. The results of an X-ray diffraction analysis of the treated crystals were compatible with theoretical simulations of an orthorhombic lattice with space group Ccmm, with zigzag chains running along the axis. The polymeric material was studied by NMR, Raman, and IR spectroscopy, and thermal expansion measurements, and all results were compatible with the assumed chain-like polymeric material. NMR showed the presence of sp\textsuperscript{3} hybridized carbon atoms forming intermolecular bonds, and IR and Raman studies showed a number of new lines, resulting from both the broken symmetries and from new, acoustic, low-frequency, intermolecular lattice vibrations in the chains (see line near 105 cm\textsuperscript{-1} in Fig. 19). Because both intermolecular bonds must form on the same side of the molecules, polymerization was also found to induce a rather strong distortion of each molecule. The success in finding a reaction route to create such well-ordered polymeric materials even from anisotropic molecules such as C\textsubscript{70} is a great step forward, which might lead to further future possibilities in creating new polymeric materials based on other heavy fullerenes.

The phase (or rather “reaction”) boundaries of the dimer and chain polymer phases have not yet been determined, and only the reaction coordinates for the two experiments reported are shown in Fig. 18. Also, for C\textsubscript{70} the drawing of a reaction map is complicated by the topochemical requirements for polymerization described above. Dimers can be formed in both fcc and hcp crystals, but ordered chain structures can only form in hcp crystals, and different initial structures thus probably also lead to different final structures. Although it has been reported that initially hcp C\textsubscript{70} reverts to fcc after high-pressure treatment (see above), it is not known which of these two structural phases is more stable under pressure and whether a change in the stacking sequence can be induced directly by pressure and/or temperature.

Fullerenes with more than 70 atoms have been very little studied under pressure. The pressure–temperature phase diagram of molecular C\textsubscript{76} was investigated up to 5 GPa near room temperature by Nakao et al. [166] but polymerization was
not observed. An attempt has also been made by Buga et al. to polymerize an en-
dohedral lanthanum compound, La@C_{82}, under a pressure of 9.5 GPa \[167\]. X-ray
and electron diffraction studies on a sample treated at 520 K showed an increased
density and disorder. Although electron diffraction showed the presence of cubic (fcc) material, the majority phase was still hcp as in the pristine sample, and
a small average decrease in lattice constant might indicate that the sample con-
tained a fraction of dimers and oligomers. Treatment at 720 K resulted in a larger
decrease in the hcp lattice constant, and electron diffraction also showed small
amounts of body-centered tetragonal phases. This sample was insoluble in
toluene and was much harder than the pristine material, indicating that poly-
merization had indeed occurred. The magnetic properties of the polymerized
material changed by about 15% relative to untreated La@C_{82}, which suggests that
the La atoms did not escape from their cages during the process.

4 Final Comments

Over the last five years, great progress has been made in our understanding of the
polymeric fullerene phases formed by treatment under high pressures and tem-
peratures. Dimer forms of both C_{60} and C_{70} have been produced in bulk amounts
and have been well analyzed, and the structures of three low-dimensional phases
of C_{60} and a quasi-one-dimensional chain phase of C_{70}, all created at relatively low
pressures and temperatures, have now been analyzed in detail by X-ray diffrac-
tion analysis of single crystals, polymerized under hydrostatic conditions. The
known reaction phase diagrams have been reinvestigated and verified in situ. For
most of these phases, a large number of microscopic and macroscopic physical
properties have already been well studied and understood, but new surprising
discoveries such as the appearance of ferromagnetism in high-pressure-treated
fullerenes \[16\] are still not well understood.

Not surprisingly, the least understood area is the field of three-dimensional
polymerization, occurring under the most severe physical conditions. A number of recent in situ studies have already provided much new information, but reach-
ing a full understanding of the structures and the physical properties of these
materials will require a large number of future studies, and although it has been
suggested \[136, 137\] that well-defined three-dimensional structures could be
assembled from two-dimensional precursors under pressure, experiments along
these lines have given little new information so far.

Other subjects of possible future interest include high-pressure studies on en-
dohedral fullerene material and on alkali-metal-doped fullerenes under pressure,
subjects not dealt with in this review, and polymerization studies on heavy
fullerenes. The fact that C_{70} has recently been shown to polymerize into a well-de-
fining chain phase \[165\] under high pressure gives hope that similar methods can
also be used to orient and polymerize pure isomers of even heavier fullerenes.

To conclude, the field of high-pressure studies on fullerenes is still alive and
well. Many interesting, and sometimes controversial, questions still await their
final answers, and many further important discoveries can probably be expected
in the near future.
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Structural and Electronic Properties of Selected Fulleride Salts

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Abstract The study of strongly correlated electron systems is at the forefront of contemporary condensed matter research because such materials, which include transition metal oxides (colossal magnetoresistive manganites, high-$T_c$ cuprates) and intermetallic heavy fermion systems, display remarkable electronic properties that challenge existing theory for satisfactory explanations. The interplay between charge, lattice, orbital and magnetic degrees of freedom in all these systems can be tuned sensitively both physically (varying an external parameter like pressure or magnetic field) and chemically (changing the chemical composition). A prominent branch of strongly correlated electron systems is the family of metal-intercalated fullerides, which display superconductivity at temperatures as high as 40 K. In this chapter, we discuss the structures and electronic and magnetic properties of selected fullerene-based architectures focusing on ammonia co-intercalated metal fullerides which are located at the boundaries of metal–insulator transitions, on alkaline-earth fullerides which deviate strongly from rigid band behaviour and on rare-earth fullerides which present unique opportunities based on the coupling between the lanthanide and fulleride electronic structures.

Keywords Fullerenes · Superconductivity · Antiferromagnetism · Metal–insulator transition · Electron correlation · Intermediate valence

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Introduction

The most well-known derivatives of C$_{60}$ are those with alkali metals, which become superconducting with high transition temperatures (up to 33 K at ambient [1], rising to 40 K at high pressure [2]). Changing the size and nature of the dopants affects sensitively the superconducting properties of the materials [3]. The high electron affinity of C$_{60}$ and the weak intermolecular van der Waals forces between the molecules in the crystal make it an excellent potential host for reductive intercalation chemistry. Indeed, intercalation of solid C$_{60}$ with electron donors, like the alkali metals, results in a wealth of intercalated fulleride salts with stoichiometries A$_x$C$_{60}$, where $x$ can be as low as 1 (RbC$_{60}$) or as high as 12 (Li$_{12}$C$_{60}$). This reflects the ease of reduction of C$_{60}$, especially to oxidation states ranging from −1 to −6.

Metallic compositions are primarily encountered for stoichiometries A$_3$C$_{60}$. These salts are superconducting and they adopt, in general, either fcc or primitive cubic structures, in which the three cations occupy the available octahedral and tetrahedral interstitial sites. Charge transfer is essentially complete and the...
conduction band of C\(_{60}\), which arises from its lowest unoccupied molecular orbital (LUMO) of \(t_{1u}\) symmetry is half filled. The fullerides are potentially simpler materials than the high-\(T_c\) cuprates and thus perhaps more easily amenable to theoretical modelling. However, they do pose many challenges, principally arising from the comparable magnitudes of the Fermi and phonon energies and the role of electronic correlations.

The study of strongly correlated electron systems like intermediate-valence heavy fermions, colossal magnetoresistive manganites and high-\(T_c\) cuprate superconductors is a key area of research in contemporary physics. C\(_{60}\)-based fullerides are also archetypal highly correlated molecular systems and the role of electron correlations is a crucial ingredient in all attempts to understand their normal and superconducting state properties, as the on-site Coulomb repulsion, \(U\), is comparable to or greater than the \(t_{1u}\) bandwidth, \(W\). Estimates of \(U\) for the C\(_{60}\) molecule are of the order of 3 eV. This value is reduced in the solid and is generally assumed to be \(\sim\)1 eV. As typical values of \(W\) for A\(_3\)C\(_{60}\) are of the order of 0.5 eV, the ratio \((U/W)\) is typically much larger than 1, so the \(t_{1u}\) band should split into two and, as a result, a Mott–Hubbard insulator should be observed [4]. For this reason, it was suggested that the metallic and superconducting behaviour in A\(_3\)C\(_{60}\) arises through the effect of non-stoichiometry, namely the true composition is A\(_3\)–\(\delta\)C\(_{60}\) [5]. However, the boundary of the metal–insulator transition shifts to a critical value of \((U/W)_{c} = 2.5\) when the triple orbital degeneracy of the LUMO states is taken into account, thus naturally accounting for the highly correlated metallic behaviour of stoichiometric A\(_3\)C\(_{60}\) [4].

Intense efforts in the last decade have exhaustively mapped the electronic and superconducting properties of intercalated alkali fullerides and the occurrence of the metal–antiferromagnetic insulator transition as a function of interfullerene separation, orientational order/disorder, valence state, orbital degeneracy, low-symmetry distortions and metal–C\(_{60}\) interactions [6–12].

2 Ammoniated Alkali Fullerides

The key experimental observation that the superconducting transition temperature, \(T_c\), of the cubic alkali fullerides, A\(_3\)C\(_{60}\), increases monotonically with the interfullerene separation (Fig. 1) [3] has driven the attempts to synthesise new fulleride salts with large lattice parameters [1, 13]. The study of such materials is fundamental in addressing the issue of whether these will be superconducting with increased \(T_c\), or whether the expected band narrowing at large interfullerene spacings will lead to electron localisation and a transition to a Mott insulator. While the on-site interelectronic repulsion, \(U\), is a molecular quantity and does not vary along the A\(_3\)C\(_{60}\) series, the width of the \(t_{1u}\) conduction band, \(W\), depends sensitively on the interfullerene separation and the ratio \((U/W)\) increases with increasing lattice constant. As a result, for large enough interball separations, \((U/W)\) may exceed the critical value of 2.5 predicted by theory [4, 14] for the transition to an insulating state. In order to locate the metal–insulator (MI) phase boundary in the electronic phase diagram of C\(_{60}\) compounds, it is necessary to synthesise systems with systematically increasing lattice constants.
Achieving large interfullerene spacings is not simple. In the cryolite-type fcc structure of the parent superconducting fullerides, A₃C₆₀, there are octahedral (one per C₆₀ unit with a radius of 2.06 Å) and tetrahedral (two per C₆₀ unit with a radius of 1.12 Å) interstices, which are occupied by the alkali cations (Fig. 2). The C₆₀–C₆₀ distance is controlled by the metal ionic size and the maximum achievable lattice expansion is limited by the maximum size of the A⁺ cations (\(r_{\text{max}} \leq r(Cs^+) = 1.69 \, \text{Å}\)) used for intercalation. However, the size of the octahedral interstices is larger than the ionic radius of any alkali ion\(^1\), allowing the possible occupation of the site by small molecular counterions or clusters that would act as structural “spacers” further expanding the fcc array. In order to maintain the metallic state and achieve higher \(T_c\), it is fundamental that the spacer used to increase the interfullerene separation should not interfere with the charge transfer as superconductivity is strongly suppressed by deviations from an exactly half-filled \(t_{1u}\) band \([15, 16]\). In addition, upon expansion, cubic symmetry should be preserved to maintain the triple orbital degeneracy of the LUMO states, which is also important in determining the consequent metallic/superconducting behaviour\(^2\).

Among different possibilities, the most obvious choice is to employ alkali ions solvated with ammonia. The NH₃ molecules are neutral and coordinate to the

---

\(^1\) The ionic radii of the alkali ions are: 0.69 Å (Li⁺), 0.95 Å (Na⁺), 1.33 Å (K⁺), 1.48 Å (Rb⁺) and 1.69 Å (Cs⁺).

\(^2\) See page 131.
Fig. 2 Cryolite structural type adopted by K$_3$C$_{60}$. Shaded and open spheres represent ions residing in octahedral and tetrahedral sites, respectively.

Fig. 3 Occupation of the octahedral site of (NH$_3$)$_4$Na$_2$CsC$_{60}$. Only one of the two possible orientations adopted by the (NH$_3$)$_4$Na$^+$ tetrahedra is shown.

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The triple orbital degeneracy of the $t_{1u}$ band plays a crucial role for the occurrence of metallic and superconducting behaviour in the A$_3$C$_{60}$ fullerides. Estimates of $U$ for the C$_{60}$ molecule are of the order of 3 eV. This value is reduced in the solid and is generally assumed to be ~1 eV. As typical values of $W$ for A$_3$C$_{60}$ are of the order of 0.5 eV, the ratio ($U/W$) is typically much larger than 1, so the $t_{1u}$ band should split into two and, as a result, a Mott–Hubbard insulating state should be observed. However, the boundary of the metal–insulator transition shifts to a critical value of ($U/W$)$_c$~2.5 when the triple degeneracy of the LUMO states is taken into account, explaining the highly correlated metallic behaviour.
alkali ions leading to large effective radii for the resulting \((\text{NH}_3)_xA^+\) species. Therefore, upon ammoniation, it is possible to achieve large interfullerene spacings without changing to a first approximation the extent of charge transfer and/or the metal–C\(_{60}\) interactions. Various families of ammoniated fullerenes, such as \((\text{NH}_3)\_K_{3-x}\text{Rb}_x\text{C}_{60} (0\leq x\leq 3)\) [17, 18], \((\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}\) [19] and \((\text{NH}_3)_x\text{Na}_2\text{A}_2\text{C}_{60}\) (\(A=K, \text{Rb}; 0.5\leq x\leq 1\)) [20] have been synthesised and characterised. Interestingly, the response of the electronic and structural properties of the fulleride salts to ammoniation is rich and varied. For instance, ammoniation of \(\text{Na}_2\text{CsC}_{60}\) results in an expansion of the cubic lattice and the metallic/superconducting state is maintained. On the other hand, the intercalation of \(\text{NH}_3\) molecules in \(K\text{C}_{60}\) produces an anisotropic expansion of the fulleride array, inducing a symmetry reduction, development of AFM long-range order below \(\sim 40\) K and suppression of the metallic state.

2.1 \((\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}\): A Lattice-Expanded Superconductor

\(\text{NH}_3\) intercalation of superconducting \(\text{Na}_2\text{CsC}_{60}\) to form \((\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}\) represents the only example of successful lattice expansion of a parent superconducting fulleride that is accompanied by an increase in \(T_c\) [19]. The cubic crystal structure is maintained and increases in size by \(\sim 0.39\) \(\text{Å}\), while \(T_c\) jumps from 10.5 to 29.6 K in accordance with the universal dependence of \(T_c\) on interfullerene separation. \((\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}\) is \text{fcc}\ (space group \(Fm\bar{3}m\), \(a=14.473\) \(\text{Å}\) at room temperature) with orientationally ordered \(\text{C}_{60}^–\) units, directly comparable with the \(Fm\bar{3}m\) structure of \(\text{Na}_2\text{CsC}_{60}\) (\(a=14.132\) \(\text{Å}\) at room temperature) [21]. The \(\text{Na(NH}_3)_4^+\) units adopt a tetrahedral geometry with the \(Na^+\) ions lying in the centre of the octahedral site and the \(N\) atoms placed along four of the possible eight body diagonals (Fig. 3). In addition, they are orientationally disordered between two possible orientations [19]. The presence of the large, almost spherical, \(\text{Na(NH}_3)_4^+\) unit (radius \(\sim 2.9\) \(\text{Å}\)) in the smaller octahedral hole (radius \(\sim 2.2\) \(\text{Å}\)) causes steric hindrance but the coordination is extremely favourable, as the tetrahedral geometry of the ion allows directional nesting of the \(\text{NH}_3\) molecules in the trigonal hole between three \(\text{C}_{60}\) units.

\((\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}\) represents a beautiful example of how to successfully increase \(T_c\) by simple lattice expansion. In this compound, the \(\text{NH}_3\) molecules act only as spacers without disrupting the cubic symmetry or interfering with the \(\text{C}_{60}–\text{C}_{60}\) and metal–\(\text{C}_{60}\) interactions. By coordinating \(\text{NH}_3\) with the \(Na^+\) ions to create a large \(\text{Na(NH}_3)_4^+\) unit, the lattice expands while all the structural and electronic properties which are fundamental for the survival of the metallic state are maintained.

2.2 \((\text{NH}_3)_x\text{Na}_2\text{A}_2\text{C}_{60}\) (\(A=K, \text{Rb}; 0.5\leq x\leq 1\)): Lattice-Expanded Fullerides with Anomalous Behaviour

The superconducting properties displayed by the series of ammoniated alkali fullerenes, \((\text{NH}_3)_x\text{Na}_2\text{A}_2\text{C}_{60}\) (\(0.5\leq x\leq 1\); \(A=K, \text{Rb}\)) differ strongly from those in \((\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}\). In these systems, \(T_c\) is dramatically lower than that expected
from the universal curve and, in addition, it increases with decreasing ammonia content, \( x \), and subsequent decreasing of the lattice dimensions, showing an unconventional trend (Fig. 4) [20, 22]. There is no crystal symmetry reduction and the structure is fcc (space group \( Fm\bar{3}m \)) with merohedrally disordered \( \text{C}_{60} \) units. The interfullerene separation is \( \sim 10.14-10.20 \) Å at 10 K, comparable to those observed in the \( \text{Rb}_{3}\text{C}_{60} \) [23] and \( \text{Rb}_{2}\text{CsC}_{60} \) [24] superconductors (\( T_c = 29 \) and 31 K, respectively), implying that the lattice expansion is not large enough to lead to sufficient band narrowing for superconductivity to be suppressed due to strong electron correlation effects. Moreover, the electronic properties of the \( (\text{NH}_3)_x\text{NaA}_2\text{C}_{60} \) (0.5\( \leq \) \( x \) \( \leq \) 1; \( A = \text{K, Rb} \)) series respond differently to chemical and physical pressure and the “universal behaviour” (\( T_c \) decreases with decreasing lattice dimensions) is recovered under the application of external pressure [25].

One possible rationale of the observed electronic properties may be associated with the highly disordered cubic structure of \( (\text{NH}_3)_x\text{NaA}_2\text{C}_{60} \). The \( \text{Na}^+–\text{NH}_3 \) pairs are disordered over the corners of two “interpenetrating” cubes centred at the octahedral holes, with the \( \text{Na}^+ \) ions and the \( \text{N} \) atoms disordered over the corners of the inner and outer cubes, respectively [26]. Each \( \text{Na}^+ \) and \( \text{N} \) atom is shifted towards three of the six neighbouring \( \text{C}_{60} \) units as they are displaced from the centre of the octahedral interstices by \( \sim 2.0 \) and \( \sim 0.5 \) Å, respectively (Fig. 5, left panel). The resulting six shortest \( \text{Na}^+–\text{C} \) distances are \( \sim 2.8 \) Å, which are comparable to those in \( \text{Na}_2\text{CsC}_{60} \) [21] and larger than the sum of the ionic radius of \( \text{Na}^+ \) and the van der Waals radius of \( \text{C} \), implying the absence of strong \( \text{Na}^+–\text{C} \) inter-

![Figure 4](image-url)  

**Fig. 4** Variation of \( T_c \) (K) with lattice parameter, \( a_o \) (Å) for various compositions of \( \text{A}_3\text{C}_{60} \). The *black triangles* show the evolution of \( T_c \) with increasing ammonia content for the \( (\text{NH}_3)_x\text{NaA}_2\text{C}_{60} \) (0.5\( \leq \) \( x \) \( \leq \) 1; \( A = \text{K, Rb} \)) series.
actions and of partial charge transfer to C$_{60}$. On the other hand, the non-bonded contacts between each H atom of NH$_3$ and the two nearest C atoms of neighbouring C$_{60}$ are in the range of 2.51–2.67 Å, and are considerably shorter than the sum of the carbon and hydrogen van der Waals radii (Fig. 5, right panel). As the C atoms involved in the short C–H contacts are those forming 6:6 bonds of C$_{60}$ which are electron rich, the structural results strongly suggest that the existence of a network of weak N–H···π(6:6) hydrogen bonding is responsible for the stabilisation of the highly disordered cubic structure. An ordered asymmetric (NH$_3$)$_2$Na$^+$ unit in the octahedral holes allows a maximum of only three N–H···π(6:6) hydrogen bonds to form while the remaining three C$_{60}$s will coordinate to Na$^+$. Such an arrangement repeated in three dimensions would lead to a reduction in symmetry. Evidently in the present compounds, disorder of the (NH$_3$)$_2$Na$^+$ units about the diagonals of the two interpenetrating [Na$_8$(NH$_3$)$_8$]$_{1/8}$ cubes allows every C$_{60}$ molecule in the structure to have an identical coordination environment and the maximum number of N–H···π(6:6) bonding interactions, while retaining cubic symmetry.

The suppression of superconductivity in (NH$_3$)$_x$Na$_2$C$_{60}$ was originally attributed to the large off-centring of the Na$^+$ ion (~2.0 Å), as C$_{60}$ would experience a non-cubic Coulomb potential causing the lifting of the $t_{1u}$ triple degeneracy and suppressing of the pairing mechanism [20, 22]. However, the Na$^+$–NH$_3$ pairs in (NH$_3$)$_2$Na$_2$C$_{60}$ are statically disordered about the diagonals of two concentric cubes and space averaging leads to maintaining the overall cubic crystal symmetry, thereby reducing the importance of such distortion effects. In addition, in order to explain the increase in $T_c$ with decreasing ammonia content, an accompanying relaxation of the Na$^+$ displacement from the centre of the octahedral hole is required, but this is not observed experimentally as there is no change in the Na$^+$–N distance for the different systems.

![Fig. 5](image)

**Left panel:** Structural model of the disordered Na(NH$_3$)$_2^+$ units which are randomly aligned along eight equivalent (111) orientations and reside in the octahedral holes of the fcc structure of (NH$_3$)$_2$Na$_2$C$_{60}$. The Na$^+$ ions and the NH$_3$ molecules are positioned at the corners of the outer and inner cube, respectively. **Right panel:** Coordination environment of a Na(NH$_3$)$_2^+$ pair in the octahedral hole of the (NH$_3$)$_2$Na$_2$C$_{60}$ crystal structure. Only one of the possible eight orientations is shown for clarity.
The structural results point to a more straightforward NH₃-specific origin of the observed non-rigid band behaviour. The structure of \((\text{NH}_3)_x\text{NaA}_2\text{C}_{60}\) is controlled by a network of hydrogen bonding \(\text{N} \cdots \text{H} \cdots \pi(6:6)\) interactions between the \(\text{Na}(\text{NH}_3)^+\) and \(\text{C}_{60}^{3-}\) units (Fig. 6), which sensitively affects electron hopping between neighbouring fullerene molecules and the electronic states near the Fermi level. As this structural motif is progressively disrupted by the partial loss of NH₃ molecules in \((\text{NH}_3)_{x<1}\text{NaA}_2\text{C}_{60}\), the shape of the conduction band resembles more that of the conventional \(t_{1u}\) superconductors and \(T_c\) rises (as the lattice contracts) towards the values expected from the “universal” relationship for the appropriate interfullerene separations. Such an ammonia-specific influence on the electronic and superconducting properties is also consistent with the high-pressure results, as physical pressure does not alter the hydrogen-bonding network for each \((\text{NH}_3)_x\text{NaA}_2\text{C}_{60}\) specific composition and only affects the size of the conduction bandwidth, thereby leading to reduced \(T_c\) upon contraction.

In the \((\text{NH}_3)_x\text{NaA}_2\text{C}_{60}\) \((0.5 \leq x \leq 1; \text{A}=\text{K}, \text{Rb})\) series, the NH₃ molecules do not simply act as spacers (cf. \((\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}\)) but substantially modify the structural and electronic properties by modulating the \(\text{C}_{60}^-\text{C}_{60}^-\) interactions. First of all, the NH₃ molecules have a stabilising effect as the parent compounds \(\text{NaA}_2\text{C}_{60}\) (\(\text{A}=\text{K}, \text{Rb}\)) do not exist. This can be understood in terms of the energetically unfavourable situation to accommodate \(\text{Na}^+\) and \(\text{K}^+/\text{Rb}^+\) in the same tetrahedral sites. Upon ammoniation, however, single-phase \((\text{NH}_3)_x\text{NaA}_2\text{C}_{60}\) phases are stabilised. The large \(\text{Na}^+-\text{NH}_3\) units of the disordered \([\text{Na}_8(\text{NH}_3)_8]_{1/8}\) clusters are now accommodated in the octahedral holes with the \(\text{K}^+/\text{Rb}^+\) ions residing in the
tetrahedral sites. This leads to steric hindrance, which favours the adoption of an fcc structure comprising merohedrally disordered C_{60}^{3–} units and no orientational phase transition is observed with temperature in analogy with K_{3}C_{60} and Rb_{3}C_{60}^{3–}. The introduction of ammonia molecules also results in the stabilisation of a novel supramolecular architecture in which each H of every NH_{3} is involved in hydrogen-bonding interactions. This gives rise to a 3D network of intermolecular interactions, which sensitively modify the electronic states of C_{60} near the Fermi level through orbital mixing, suppress electron hopping between neighbouring fulleride ions and lead to an increased conduction bandwidth.

2.3
(NH_{3})K_{3}C_{60}: Lattice Expansion and Symmetry Lowering

2.3.1
Electronic and Magnetic Properties

In both (NH_{3})_{4}Na_{2}CsC_{60} and (NH_{3})_{2}NaA_{2}C_{60} (A=K, Rb) families, the introduction of NH_{3} results in lattice expansion but the values of interfullerene separations are still below that of RbCs_{2}C_{60}. This implies that the (U/W) ratio is smaller than the critical value of 2.5 and all these systems lie on the metallic side of the A_{3}C_{60} electronic phase diagram. When K_{3}C_{60} is intercalated with NH_{3} to afford (NH_{3})K_{3}C_{60}, the C_{60}^{3–} array expands again but the interfullerene separation increases from 10.05 to 10.57 Å, now exceeding the value for RbCs_{2}C_{60} (10.29 Å) [17]. Despite the universal Ti–interfullerene spacing relation predicting a superconducting transition at about 33 K, (NH_{3})K_{3}C_{60} is not superconducting. In addition, the lattice expansion is anisotropic and the symmetry is reduced to orthorhombic.

The nature of the electronic state of (NH_{3})K_{3}C_{60} has been investigated extensively. Early magnetic susceptibility, EPR and {^{13}}C NMR measurements described it as a narrow band metal which exhibits a transition to an insulating ground state at ~40 K [27, 28]. The nature of the low-temperature state remained con-

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3 By comparing the radii of the alkali ions with the sizes of the available interstices in the A_{3}C_{60} fcc structure, we see that the octahedral hole is large enough to accommodate all ions, while the tetrahedral one has a size larger than Na^{+} but smaller than K^{+}. As a result, the size of the alkali ions occupying the tetrahedral voids plays a crucial role in determining the structural properties, and different behaviour is observed between alkali fullerides containing large alkali ions (Cs^{+}, Rb^{+}, K^{+}) and those containing the smaller Na^{+} and Li^{+}. In the first case, the structure is best described in space group Fm\bar{3} m with a unit cell size larger than that of C_{60} (14.24 Å for K_{3}C_{60}). The fulleride ions are not free to rotate, as in the case of pure C_{60}, due to steric effects associated with the alkali ions in the tetrahedral sites. Instead, they are merohedrally disordered and adopt two equally populated orientations related by a 90° rotation about the [001] or equivalently by 44°23′ about the [111] crystal axis. No phase transition driven by changes in the reorientational behaviour occurs as a function of temperature. In the second case, as the Na^{+} radius is smaller than the size of the tetrahedral hole, there is enough space for the C_{60}^{3–} ions to rotate in such a way as to optimise the Coulomb interactions. The resulting structure is also fcc, but the C_{60}^{3–} ions are now quasi-spherically disordered. On cooling, a phase transition occurs in the vicinity of room temperature to a primitive cubic structure (space group Pa\bar{3}).
troversial, as the experimental results were unable to distinguish between magnetic (AFM, SDW) or non-magnetic (CDW) ground states. The existence of non-zero internal local magnetic fields at low temperature in (NH₃)K₃C₆₀ was addressed by using 100% spin-polarised positive muons (μ⁺) [29]. In the presence of local magnetic fields, ⟨Bₘ⟩, these precess with a frequency νₘ=(γ/2π)⟨Bₘ⟩, where γ/2π=13.55 kHz/G. In the absence of an applied external field, the appearance of a precession signal implies the onset of an ordering (ferromagnetic or AFM) transition.

The time dependence of the ZF μ⁺ spin polarisation for (ND₃)K₃C₆₀ at temperatures higher than 40 K shows only a non-oscillating signal (Fig. 7). In this temperature range, the μ⁺ spin relaxation is determined by the fluctuations of the nuclear moments, which appear frozen into a disordered spin configuration. Below 40 K, the shape of the time-dependent μ⁺SR spectra changes and a short-lived oscillating component, whose depolarisation gradually increases with decreasing temperature, appears (Fig. 7). The observation of a precession signal in ZF is clear evidence of the existence of coherent ordering of the electronic spins and indicates unambiguously the onset of long-range AFM order. The static local field at the muon site, ⟨Bₘ⟩, is 42 G at 14 K, while the distribution of the local fields has a width, ⟨ΔB²⟩/2 of 25 G, only smaller than ⟨Bₘ⟩ by a factor of 1.7.

The temperature evolution of the muon frequency, νₘ, is described by νₘ=ν₀ [1–(T/T_N)]^β, with ν₀=0.64(1) MHz, T_N=36.5(3) K and β=0.32(3). The critical exponent, β, is close to the value expected for a conventional 3D Heisenberg AFM (β=0.36). As the μ⁺ site is not known for a powder sample, a value of the magnetic moment cannot be extracted directly. However, as ν₀ is 1.4 times smaller than the

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**Fig. 7** Evolution of the zero-field (ZF) μ⁺ spin polarisation, Pₘ(t) at 14 and 40 K for (ND₃)K₃C₆₀
frequency observed in the ferromagnet (TDAE)C\textsubscript{60} (~0.92 MHz), in which the magnetic moment is ~1 \( \mu_B \)/molecule [30, 31], and assuming similar stopping sites for the two samples, \( \mu(0 \text{ K}) \) is ~0.7 \( \mu_B \)/molecule.

The \( \mu^+ \)SR measurements clearly showed that (NH\textsubscript{3})K\textsubscript{3}C\textsubscript{60} undergoes a transition below ~37 K to a LRO AFM state, which was also confirmed by subsequent EPR and \(^{13}\text{C}, \, ^{1}\text{H- and }^{39}\text{K-} \)NMR experiments [32, 33]. However, in disagreement with earlier ESR and NMR results, Tou et al. [33] concluded that the material is an insulator even above 40 K. This was also confirmed by a microwave conductivity study which revealed that (NH\textsubscript{3})K\textsubscript{3}C\textsubscript{60} is insulating above the AFM transition with a conductivity value at 200 K 3–4 orders of magnitude smaller than that of superconducting K\textsubscript{3}C\textsubscript{60} [34]. The absence of a MI transition at \( T_N \) then rules out magnetic ordering as an explanation for the loss of superconductivity and suggests that the Mott–Hubbard state in (NH\textsubscript{3})K\textsubscript{3}C\textsubscript{60} is related to the non-cubic crystal symmetry [35]. The orthorhombic symmetry lifts the degeneracy of the \( t_{1u} \) orbitals and the critical value of the \( (U/W) \) ratio for the transition to the AFM Mott insulating state decreases to values lower than 2.5.

2.3.2 Crystal Structure at Ambient Pressure

The room-temperature crystal structure of (NH\textsubscript{3})K\textsubscript{3}C\textsubscript{60} was first determined by Rosseinsky et al. [17]. Ammoniation of K\textsubscript{3}C\textsubscript{60} leads to an orthorhombic distortion of the fcc structure with one K\textsuperscript{+} and one NH\textsubscript{3} per octahedral site. The C\textsubscript{60} units are orientationally ordered with their two-fold axes aligned with the unit cell vectors (space group \textit{Fmmm}), while K\textsuperscript{+} and NH\textsubscript{3} are oppositely displaced from the site centre along the [110] direction and the K\textsuperscript{+}–NH\textsubscript{3} pairs are randomly oriented along one of four K\textsuperscript{+}–NH\textsubscript{3} directions.

Further X-ray diffraction work revealed a second-order phase transition at 150 K, attributed to an orientational order–disorder transition of the K\textsuperscript{+}–NH\textsubscript{3} pair at the octahedral site [36]. The low-temperature orthorhombic structure (space group \textit{Fddd}) is derived by doubling the lattice constants of the high-temperature phase along all three axes, with the K\textsuperscript{+}–NH\textsubscript{3} pairs orienting along the [110] direction and the K\textsuperscript{+}–NH\textsubscript{3} pairs orienting along the [110] direction in an antiferroelectric fashion.

Subsequently, neutron powder diffraction measurements on perdeuterated (ND\textsubscript{3})K\textsubscript{3}C\textsubscript{60} identified precisely the C\textsubscript{60} geometry and orientation together with the location of the ammonia molecules and their coordination environment [37]. In addition to the K\textsuperscript{+}–NH\textsubscript{3} pair ordering, there is also a unique orientational ordering motif of the C\textsubscript{60} units (Fig. 8). An ordered superstructure of K\textsubscript{3}C\textsubscript{60} in which the C\textsubscript{60} orientation alternates from every (001) plane to the next (space group \textit{P4\textsubscript{2}/mnm}), has been discussed theoretically but not observed experimentally [38]. The orientational ordering pattern in (ND\textsubscript{3})K\textsubscript{3}C\textsubscript{60} is such that C\textsubscript{60} molecules located at (0,0,0) and (1/2,1/2,1/2) adopt two different orientations. While the units at the origin are all oriented with the 6:6 C–C bond parallel to the \( b \) axis (orientation I), those at (1/2,1/2,1/2) have the 6:6 C–C bond parallel to \( a \) (orientation II). The pattern produced is that of 2D sheets of C\textsubscript{60}, which order ferrorotationally (orientation I) along [110] and antiferrorotationally (orientations I and II) along [1–10] and which stack alternately along the \( c \) axis. There is a remark-
Fig. 8  Projection of the low-temperature face-centred orthorhombic structure of (NH₃)K₃C₆₀ on the [110] basal plane. The antiferroelectric ordering of the K⁺–NH₃ pairs is shown together with the ferriorotative (antiferriorotative) order of C₆₀ along the base diagonal (110)/(1–10).

able correlation of this superstructure with the 3D AFM structure derived from NMR experiments (Fig. 9) [33]. In the latter, the C₆₀ units along [110] order antiferromagnetically, while those along [1–10] order ferromagnetically. Thus the nature of the intermolecular magnetic exchange interactions sensitively depends on the relative orientation of near-neighbour C₆₀ units. In the Fddd orthorhombic superstructure, the 6:5 C–C bonds face each other when viewed along the centre-to-centre direction, but the existence of a centre of inversion along [110] leads to pentagonal faces directed over hexagons and vice versa. In contrast, along [1–10], pentagonal (hexagonal) faces of near neighbours align over pentagons (hexagons). The observed ordering pattern is reminiscent of that proposed theoretically to account for the development of ferromagnetism in (TDAE)C₆₀ [39, 40].

These experimental observations point to the fundamental role played by the C₆₀ orientational degrees of freedom in determining the electronic and magnetic response of (NH₃)K₃C₆₀. The orientational ordering motif gives rise to distinct orbital ordering that modulates the intermolecular exchange interactions (Fig. 10). This strong coupling among the orbital, charge, spin and lattice responses is reminiscent of the behaviour of other strongly correlated systems such as the CMR manganese oxides. Temperature-dependent diffraction measurements on (ND₃)K₃C₆₀ showed that the orientational ordering temperature (~150 K) is higher than Tₐ, suggesting that the former is the driving force for the magnetic ordering.
Crystal Structure at High Pressure

The suppression of superconductivity in (NH$_3$)$_3$K$_3$C$_{60}$ has been attributed to the crystal symmetry lowering that lifts the $t_{1u}$ orbital degeneracy and decreases the $(U/W)_c$ ratio for the transition to the AFM Mott insulating state. This is aided by the increased inter fullerene separation (10.57 Å) in the $ab$ plane (substantially larger than the value of 10.05 Å found in K$_3$C$_{60}$), which reduces the bandwidth, $W$, and increases further ($U/W$).

However, the application of pressure ($P>1$ GPa), which reduces the C$_{60}$–C$_{60}$ spacing, leads to recovery of superconductivity with $T_c=28$ K (Fig. 11) [41]. The crystal symmetry of (NH$_3$)$_3$K$_3$C$_{60}$ at high pressure and the reasons for which superconductivity is recovered are thus of great importance. A synchrotron X-ray structural study as a function of pressure at ambient temperature showed that above 0.8 GPa, there is a phase transition from orthorhombic $Fmmm$ (isostructural with the ambient-pressure high-temperature phase) to orthorhombic $Fddd$ (isostructural with the ambient-pressure low-temperature phase) [42]. The evolution of the lattice constants with pressure reveals strongly anisotropic compressibility. The most compressible axis is $b$, while $c$ and $a$ show almost the same compressibility. While at ambient pressure the structure of (NH$_3$)$_3$K$_3$C$_{60}$ is pseudotetragonal ($a\sim b$), increasing pressure results in increased orthorhombic distortion. The implication of these results is that the superconducting phase of (NH$_3$)$_3$K$_3$C$_{60}$ retains a strongly distorted orthorhombic structure. The lifting of the $t_{1u}$ orbital degeneracy is thus not sufficient to keep the system on the insulating side of the metal–insulator transition. The nearest-neighbour inter fullerene separation in

![Diagram](image-url)
the $ab$ plane shortens by $\sim 1.6\%$ between ambient pressure and 1.2 GPa. The resulting separation of 10.40 Å is comparable to that observed in cubic RbCs$_2$C$_{60}$ [24] and evidently leads to sufficient broadening of the conduction band to allow recovery of metallic behaviour and superconductivity at 28 K. The high-pressure phase of (NH$_3$)K$_3$C$_{60}$ is the only non-cubic superconductor among $t_{1u}$-based fullerides. Low-symmetry superconducting phases are more abundant among $t_{1g}$-based systems, which are characterised by broader conduction bands and non-rigid band behaviour arising from the strong mixing of metal and carbon orbitals (Sect. 3.1).

2.4 (NH$_3$)K$_3$C$_{60}$ and (NH$_3$)NaRb$_2$C$_{60}$: Molecular and Lattice Vibrations

Inelastic neutron scattering (INS) measurements have been successfully used to study dynamical phenomena such as molecular or lattice vibrations in pristine C$_{60}$ [43] and a variety of fullerides [44–48]. When INS spectra are collected on instruments with a large energy window, it is possible to observe all phonon modes including the molecular vibrations and the generalised phonon density-of-states (GDOS) can be directly calculated.

The GDOS of (NH$_3$)K$_3$C$_{60}$ [49] between 0 and 70 meV is dominated by non-C$_{60}$ vibrational modes involving hydrogen motion and shows the presence of three

![Schematic diagram of orientational and magnetic order in the basal plane of the (NH$_3$)K$_3$C$_{60}$ structure. Shaded (open) circles denote orientation I (II) of C$_{60}$. The moment directions have yet to be determined and are arbitrarily placed parallel to the b-axis.](image-url)
temperature-independent broad peaks at 4 (lattice vibrations), 12 (NH3 torsions) and 35 meV (N–K–N δ bending modes). Below 150 K, a new sharp peak appears at 6.5 meV, growing in intensity with decreasing temperature. This librational peak is associated with the structural transition at 150 K when the K⁺–NH3 pairs order antiferroelectrically and provides the signature of the freezing of the NH3 rotation. While at high temperature the K⁺–NH3 pairs are randomly oriented with dynamically changing directions, below 150 K their motion freezes and they now perform small-amplitude librational motion around their threefold axis.

The GDOS of (NH₃)NaRb₂C₆₀ [50] at 300 K shows features at 9, 25, 35, 50, 70 and 95 meV (Fig. 12). The peaks above 50 meV are assigned to the intramolecular modes of C₆₀, while the low-energy ones are attributed to torsional modes of NH₃ (9, 25 meV) and to N–Na–N δ bending modes (35 meV). Again below 150 K, major differences are evident in the low-energy spectral part (Fig. 12). A new peak centred at 5.5 meV appears and grows in intensity with decreasing temperature, while the feature at 9 meV sharpens. These changes are associated with the librational motion of NH₃ although no structural phase transition is observed in (NH₃)NaRb₂C₆₀ with decreasing temperature, unlike (NH₃)K₃C₆₀. At high temperatures, NH₃ behaves as a free rotor and the Na⁺–NH₃ units are dynamically disordered along the diagonals of the two interpenetrating [Na₈(NH₃)₈]₁/₈ cubes centred at the octahedral site [26]. With decreasing temperature NH₃ is trapped in a torsional potential, which is somewhat larger than that in (NH₃)K₃C₆₀ where
no 3D network of hydrogen-bonding interactions is present. The sharpening of the peak at 9 meV with decreasing temperature may be attributed to the strengthening of the H-bonding network.

INS is also an ideal technique to study quantum rotational tunnelling transitions\(^4\) in crystalline samples that are directly observed as inelastic peaks in the \(\mu\)eV range at low temperatures. A variety of information can be extracted from tunnelling spectra measured with neutrons, such as the strength and shape of the hindering rotational potential and the site multiplicities in the crystal structure [51–54]. Indeed the INS spectrum of (NH\(_3\))K\(_3\)C\(_60\) at 1.5 K is dominated by an intense broad (HWHM=66(5) \(\mu\)eV) band centred at \(\Delta E=354(5)\) \(\mu\)eV (Fig. 13) [55]. Its shape is strongly asymmetric with a shoulder on the low-energy side and another not well-resolved band present on the high-energy side. With increasing temperature the main line at 354 \(\mu\)eV weakens in intensity, shifts towards lower energies and broadens considerably. At the same time, the other two excitations become gradually less pronounced until at 19 K, they are no longer discernible. At 70.4 K, all inelastic features have completely disappeared and only a quasi-elastic component remains. The INS excitations in (NH\(_3\))K\(_3\)C\(_60\) are assigned to rotational tunnelling transitions of the NH\(_3\) molecules.

The simplest potential that we can use to interpret the measured tunnelling spectra is a 1D torsional potential with threefold symmetry, \(V_3\). For this, the principal tunnelling energy between the rotational ground and the first excited state

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\(^4\) Quantum rotational tunnelling of symmetric molecules is well established in the solid state. Rotational tunnelling describes the phenomenon of the librational states of a molecule whose rotating atoms are indistinguishable being multiplets. The size of the splitting between the sub-states (tunnel splitting) is determined by the inertial properties of the molecule and the type and strength of the rotational potential. Large detectable splittings are found for molecules with a large rotational constant, \(B=\hbar^2/2I\), where \(I\) is the moment of inertia (e.g. linear H\(_2\) \((B=7.3\) meV), symmetric top CH\(_3\) \((B=0.655\) meV) and NH\(_3\) \((B=0.782\) meV), and spherical NH\(_4^+\) \((B=0.655\) meV)). For most other molecules, \(B\) is of the order of 0.1 K or less.
Fig. 13  Representative INS spectra of (NH₃)K₃C₆₀ at 1.5 K (left panel) and of (NH₃)NaRb₂C₆₀ at 4 K (right panel) at an average scattering vector, \( Q = 0.84 \ \text{Å}^{-1} \). The *open circles* are experimental points and the *lines* are best fits. The *dashed lines* show the individual components at both zero and non-zero energy transfer.
(\(J=0 \rightarrow 1\)) corresponds to a potential barrier, \(V_3 \sim 5.7\) meV. The higher-energy rotational transitions are predicted at 3.8 (\(J=0 \rightarrow 2\)), 6.3 (\(J=0 \rightarrow 3\)), 7.0 (\(J=0 \rightarrow 4\)) and 11.1 meV (\(J=0 \rightarrow 5\)), in good agreement with features observed in the GDOS of \((\text{NH}_3)\text{K}_3\text{C}_{60}\). Structural analysis showed that each \(\text{K}^+\text{–NH}_3\) pair is displaced from the centre of the octahedral interstices experiencing an anisotropic environment. Thus, while the majority of the rotors are ordered with their rotation axes aligned on the basal plane and experience a hindrance potential with a barrier of 5.7 meV, the strong anisotropy of the environment leads to a distribution of hindering sites, thereby accounting for the substantial width of the tunnelling peak. The appearance of the low-energy shoulder (\(\sim 240\) meV) likely arises from partial precessional disorder of the \(\text{K}^+\text{–NH}_3\) bond about \(\langle 110 \rangle\), as this leads to a stronger trapping potential (\(\sim 8\) meV). The origin of the high-energy peak at \(\sim 590\) \(\mu\)eV is also of interest, as it implies quasi-free rotational motion of \(\text{NH}_3\) under the influence of a much weaker potential (\(\sim 2\) meV). An attractive explanation for this peak, whose intensity is only \(\sim 10\%\) of the main tunnelling peak, is an incomplete transformation to the antiferroelectrically ordered phase with some \(\text{NH}_3\) molecules remaining in a disordered state to low temperatures. This is supported by \(^1\text{H}\) NMR data on \((\text{NH}_3)\text{K}_3\text{C}_{60}\) which find the presence of a \(\sim 20\%\) impurity phase at low temperatures [33].

Quantum rotational tunnelling transitions were also present in the INS spectrum of \((\text{NH}_3)\text{NaRb}_2\text{C}_{60}\) at 4 K (Fig. 13) [50]. An intense, quite symmetric, broad peak is centred at 330(6) \(\mu\)eV, softening by \(\sim 35\%\) and broadening by \(\sim 122\%\) between 4 and 50 K. For a 1D torsional potential with threefold symmetry, the observed tunnelling energy corresponds to a potential barrier, \(V_3 \sim 6.1\) meV for the \(J=0 \rightarrow 1\) transition. In \((\text{NH}_3)\text{NaRb}_2\text{C}_{60}\) at these low temperatures, all rotors are disordered along the diagonals of two interpenetrating \([\text{Na}_8(\text{NH}_3)_8]_{1/8}\) cubes; due to the cubic symmetry of the structure, they all experience the same torsional hindrance potential of 6.1 meV, independently of the orientation adopted at each site. However, the displacement of the \(\text{NH}_3\) molecules from the centre of the site creates a certain degree of anisotropy, which may account for the substantial width of the tunnelling peak.

Low-energy INS measurements were also employed to study the orientational dynamics of \(\text{C}_{60}\) in \((\text{ND}_3)\text{K}_3\text{C}_{60}\) [56]. Well-defined excitations are observed with energy varying between 3.11(7) and 2.38(5) meV, as the temperature increases from 30 to 310 K (Fig. 14). The \(Q\) dependence of their intensities is consistent with their assignment to small-amplitude librational motion of the \(\text{C}_{60}\) ions. The librations in \((\text{ND}_3)\text{K}_3\text{C}_{60}\) are both softer and broader than those in the parent fulleride \(\text{K}_3\text{C}_{60}\) [44], reflecting the existence of a weaker and more anisotropic orientational potential upon ammoniation. The estimated barrier of the hindrance potential, \(E_\alpha \sim 250\) meV, is approximately half the size of that in \(\text{K}_3\text{C}_{60}\) and comparable to that found in the primitive cubic fulleride \(\text{Na}_2\text{RbC}_{60}\) [45]. The temperature dependence of the energies and widths of the librational peaks in \((\text{ND}_3)\text{K}_3\text{C}_{60}\) is also more reminiscent of the behaviour of \(\text{Na}_2\text{RbC}_{60}\) rather than \(\text{K}_3\text{C}_{60}\).

The librational energies of cubic fullerides scale with the size of the ion, \(r_A\), occupying the tetrahedral interstices in the cubic lattice. When \(r_A < 1.12\) Å, the low-temperature structure is primitive cubic (space group \(\text{Pa}3\)) [21] and the li-
Fig. 14 Representative INS spectra of (ND$_3$)K$_3$C$_{60}$ in the temperature range 30–100 K at constant $Q=5.5$ Å$^{-1}$. The solid circles are experimental points and the solid lines are best fits.

The librational energy is roughly constant at $\sim2.8$ meV (e.g. Na$_2$RbC$_{60}$, Na$_2$CsC$_{60}$). However, when $r_A>1.12$ Å, the structure is fcc and the librational energy increases almost linearly with increasing $r_A$ (e.g. K$_3$C$_{60}$, Rb$_3$C$_{60}$). Such behaviour reflects the dominance of the repulsive $A^+–C_{60}^3$ overlap in determining the orientational potential in these systems. In the case of (ND$_3$)K$_3$C$_{60}$, ammoniation leads to a reduction in crystal symmetry and an anisotropic expansion of the unit cell to accommodate the large K$^+–NH_3$ units in the octahedral interstices. As a result, the size of the tetrahedral hole also becomes considerably larger, expanding to $r_t=1.28$ Å. So in order to rationalise the measured characteristics of the orientational potential in (ND$_3$)K$_3$C$_{60}$, the low-temperature librational energies are plotted as a function of the ratio of $r_A$ to the size of the tetrahedral hole, $r_t$ (Fig. 15). When $(r_A/r_t)<1$, the librational energy is roughly constant at $\sim2.8$ meV, but when $(r_A/r_t)>1$, it increases linearly with increasing $(r_A/r_t)$. From these considerations, one can explain the observed differences (similarities) between the
Fig. 15  Schematic diagram showing the dependence of the low-temperature librational energy on \((r_A/r_t)\), where \(r_t\) is the size of the tetrahedral hole and \(r_A\) is the radius of the ion residing in it orientational potentials in \((\text{ND}_3)\text{K}_3\text{C}_{60}\) and \(\text{K}_3\text{C}_{60}\) (\(\text{Na}_2\text{RbC}_{60}\)) in terms of simple crystal packing considerations and the continued importance of the repulsive \(\text{A}^+–\text{C}_{60}^3–\) interactions. The introduction of ammonia in the \(\text{K}_3\text{C}_{60}\) structure brings about an increase in the size of the tetrahedral hole by \(~0.16\) Å and reduces \((r_A/r_t)\) from 1.23 in \(\text{K}_3\text{C}_{60}\) to 1.08, close to the value of 1 in \(\text{Na}_2\text{RbC}_{60}\).

### 2.5 \((\text{NH}_3)\text{K}_{3–x}\text{Rb}_x\text{C}_{60}\) \((0 < x \leq 3)\): Pushing Lattice Expansion to the Limit

Attempts to increase further the interfullerene separation by substituting Rb at the K sites of \((\text{NH}_3)\text{K}_3\text{C}_{60}\) resulted in the family of fullerides, \((\text{NH}_3)\text{K}_{3–x}\text{Rb}_x\text{C}_{60}\) \((0 < x \leq 3)\) [18]. In analogy with \((\text{NH}_3)\text{K}_3\text{C}_{60}\), all members undergo an AFM transition with \(T_N\) strongly depending on the Rb concentration, \(x\): first \(T_N\) increases to 76 K for \(x=2\) and then decreases to 58 K for \(x=3\) (Fig. 16). The observed trend is at first sight reminiscent of the phase diagram anticipated for a Mott–Hubbard system in which there is a crossover from itinerant to localised behaviour with increasing \(U/W\); as \(T_N\) should increase with increasing interfullerene separation in the metallic regime and decrease in the localised regime. However, all \((\text{NH}_3)\text{K}_{3–x}\text{Rb}_x\text{C}_{60}\) \((0 \leq x \leq 3)\) solids are insulating below 250 K with no MI transitions observed [34]. This poses a considerable challenge in understanding the electronic properties, as a simple localised moment model necessitates a reduction of \(T_N\) with increasing interfullerene separation (decreasing exchange interaction, \(J\)) rather than the complex behaviour observed experimentally.
Fig. 16  Schematic electronic phase diagram of C₆₀³⁻ compounds, including the evolution of the Néel temperature, $T_N$ (open squares) for the family $(\text{NH}_3)_3\text{Rb}_x\text{C}_60$ ($0 \leq x \leq 3$)

At room temperature, $(\text{NH}_3)_3\text{Rb}_x\text{C}_60$ ($0 < x \leq 3$) are isostructural with $(\text{NH}_3)_3\text{C}_60$ (space group $Fmmm$) and undergo an orientational order–disorder transition below 150 K. At first sight, the low-temperature phases appear to adopt the $Fddd$ superstructure of $(\text{NH}_3)_3\text{C}_60$ (Sect. 2.3.2). However, the evolution of the lattice constants with increasing Rb content is not monotonic and $(\text{NH}_3)_3\text{Rb}_3\text{C}_60$ shows anomalous lattice size, necessitating further structural considerations. In $(\text{NH}_3)_3\text{C}_60$, the $\text{K}^+–\text{NH}_3$ pairs in the $a_0 b_0$ basal plane order antiferroelectrically along the [110] direction. The stacking sequence along $c_0$ can be generated using the glide vectors $1/4(\pm a_0 \pm c_0)$ and $1/4(\pm b_0 \pm c_0)$, thereby resulting in $\text{K}^+–\text{NH}_3$ chains rotated by 90° in consecutive planes along $c_o$ (perpendicular ordering model) [36]. However, there is also an alternative stacking sequence in which the $\text{K}^+–\text{NH}_3$ units are aligned parallel in consecutive planes along $c_0$. Such an ordering scheme can be described with the monoclinic space group $I2/a$ (space group $C2/c$, cell choice 3), obtained by a direct transformation of the $F$-centred orthorhombic supercell using the relationships: $a_m \sim c_o$, $b_m \sim c_m \sim 1/2(a_o^2+b_o^2)^{1/2}$, $\beta_m \sim 90^\circ$. In this cell, the $\text{K}^+–\text{NH}_3$ pairs in the $b_m c_m$ plane align antiferroelectrically along the [010] direction (parallel ordering model). The stacking sequence along $a_m$ can then be generated using the glide vectors $1/4(\pm a_m \pm b_m)$ and $1/4(\pm a_m \pm c_m)$. Rietveld refinements of synchrotron X-ray diffraction data have now clearly shown that, while at low temperature $(\text{NH}_3)_3\text{K}_{3-x}\text{Rb}_x\text{C}_60$ ($x=0, 1, 2$) adopt the perpendicular ordering model, parallel ordering of $\text{Rb}^+–\text{NH}_3$ is found for $(\text{NH}_3)_3\text{Rb}_3\text{C}_60$ (lattice constants at 10 K: $a_m=27.157(1)$ Å, $b_m=21.274(1)$ Å, $c_m=21.434(1)$ Å, $\beta_m=90.02(1)^\circ$).

The evolution of the structural behaviour of $(\text{NH}_3)_3\text{Rb}_x\text{C}_60$ with increasing $x$ raises many questions. Along the series there is a certain critical composition, $x_c=2$, for which it becomes favourable to adopt a parallel alignment of the $\text{Rb(K)}^+–\text{NH}_3$ pairs. Above $x_c$, contraction instead of expansion of the stacking
axis is observed with increasing Rb content. For compositions \(x\) between 2 and 3 some of the ammonia molecules coordinate with the larger Rb\(^+\) ions within the pseudo-octahedral site. The NH\(_3\) coordination with Rb\(^+\) is weaker than with K\(^+\) and this is reflected in longer Rb\(^+\)–N distances (2.85 Å compared to 2.48 Å for K\(^+\)–N) and a subsequent larger displacement of the cation from the centre of the site. Within the perpendicular alignment model the Rb\(^+\)–C\(_{60}\) contacts reach values as short as 2.9 Å. Instead, in the parallel model the steric hindrance is released with all Rb–C distances ~3.2–3.3 Å. In addition, the parallel configuration allows optimisation of the Coulomb interactions between Rb\(^+\)–NH\(_3\) dipoles, resulting in smaller distances between pairs on subsequent planes and a contraction of the stacking axis.

From these structural considerations, we conclude that the monoclinic C\(_2/c\) model with parallel orientation of the Rb(K)\(^+\)–NH\(_3\) dipoles represents the optimised structural model where the steric hindrance and the attractive–repulsive interactions are minimised. However, the compositions with \(x<2\) adopt the less favourable Fddd model where the pairs align perpendicularly. Possible explanations could be found by taking into consideration the influence of the intermolecular interactions. In the C\(_2/c\) model, no hydrogen-bonding network is found either along the stacking axis or in the bc planes. However, when the smaller K\(^+\) ion coordinates with NH\(_3\), there is enough space for the pair to rotate in such a way as to optimise the intermolecular interaction pattern. In the Fddd model, a 2D network of hydrogen-bonding interactions is found in the (110) planes.

The progressive disruption of the hydrogen-bonding network with increasing Rb content could also be related to the anomalous dependence of \(T_N\). In insulating (NH\(_3\))Rb\(_3\)C\(_{60}\), there is no intermolecular interaction network which could influence the magnetic exchange and \(J\) is only modulated by the interfullerene separation. In (NH\(_3\))K\(_3\)C\(_{60}\), which is also insulating at all temperatures, \(T_N\) should be higher than in (NH\(_3\))Rb\(_3\)C\(_{60}\) as the lattice dimensions are smaller. Instead \(T_N\) is lower, implying that the presence of the 2D hydrogen-bonding network has a detrimental effect on the magnetic exchange by modulating the orbital overlap between nearest-neighbour (nn) C\(_{60}\) units. Furthermore, a closer look at the 2D intermolecular interaction pattern for (NH\(_3\))K\(_3\)C\(_{60}\) shows that only the C\(_{60}\) units which adopt orientation I are involved in hydrogen-bonding interactions. It is thus possible to relate all the factors which control the electronic and magnetic properties in (NH\(_3\))K\(_3\)C\(_{60}\): namely, the orientational ordering pattern of the C\(_{60}\) units, the 3D AF structure and the network of intermolecular interactions. Hydrogen bonding mainly affects the nn C\(_{60}\) along (110), which is precisely the direction of AF coupling. The AF magnetic exchange is strongly influenced resulting in a suppressed value for \(T_N\). Increasing the Rb content \(x\) to 2 causes expansion of the ab planes. Consequently, the hydrogen-bonding interactions become less effective and \(T_N\) increases. For \(x>2\), the Rb–NH\(_3\) pairs adopt parallel orientations due to steric hindrance, the hydrogen-bonding network disappears and \(T_N\) now decreases according to the simple localised moment model.
3 Alkaline-Earth and Rare-Earth Fullerides

3.1 Superconductivity in Alkaline-Earth Fullerides

Intercalation of C$_{60}$ by alkaline-earth metals was first performed by Kortan and co-workers for Ca, Sr and Ba. Superconductivity with $T_c$=8 K was reported for Ca$_5$C$_{60}$ [57]. The superconducting phase is fcc-derived, but its detailed structure remains to be established. It was also reported that Ba$_6$C$_{60}$ and Sr$_6$C$_{60}$ were superconducting [58, 59]. Later careful experiments proved that the true superconducting phases are the body-centred orthorhombic (bco) Sr$_4$C$_{60}$ and Ba$_4$C$_{60}$. Baenitz et al. showed that the superconducting phase of Ba-doped C$_{60}$ could be orthorhombic [60]. However, since it was only in a minority, phase identification was not conclusive. In 1999, synthesis of single-phase orthorhombic Ba$_4$C$_{60}$ showed unambiguously bulk superconductivity at $T_c$=6.7 K [61]. Ba$_4$C$_{60}$ is the first fully characterised non-cubic superconductor without fcc arrangement of C$_{60}$ units.

A schematic representation of the structures of Ba$_x$C$_{60}$ ($x$=3, 4, 6) is shown in Fig. 17. In contrast to fcc K$_3$C$_{60}$, Ba$_3$C$_{60}$ forms an A15-type structure with a body-centred arrangement of C$_{60}$ molecules. At $x$=4 and 6, both K$_x$C$_{60}$ and Ba$_x$C$_{60}$ adopt body-centred structures. The transformation from face-centred to body-centred structures with increasing doping level is a generic feature of metal fullerides, but the structural difference between Ba$_3$C$_{60}$ and K$_3$C$_{60}$ provides an example of the dependence on the metal ionic radius and the valence of C$_{60}$. When one takes a closer look at the orientational states, the structures of A$_4$C$_{60}$ (A=K, Rb) and Ba$_4$C$_{60}$ differ from each other. In the bct structure of K$_4$C$_{60}$ and Rb$_4$C$_{60}$ (space group I$4/mmm$) [62], the C$_{60}$ units are merohedrally disordered. In Ba$_4$C$_{60}$, on the other hand, the molecules are fully ordered and the Immm space group is adopted [61]. This structure is identical to that of Cs$_4$C$_{60}$, where the increase of metal–fullerene interaction due to the large ionic radius leads to complete orientational ordering [63]. Though the ionic radius of Ba$^{2+}$ is identical to that of K$^+$, the larger Madelung energy due to the increased ionicity induces contraction of the lattice parameter and full orientational ordering. For $x$=6, the C$_{60}$ units are orientationally ordered both in the alkali [64] and the alkaline-earth compounds [59], and thus the structures of M$_6$C$_{60}$ are identical for M=K, Rb, Cs, Sr and Ba.

![Schematic structures of Ba-intercalated C$_{60}$ compounds](image17.png)

Fig. 17 Schematic structures of Ba-intercalated C$_{60}$ compounds
The left panel of Fig. 18 shows the Raman spectra of pristine and Ba-intercalated C₆₀ [65]. The strongest peak at ~1400 cm⁻¹ is assigned to the tangential mode, A₈(2), of C₆₀ which is a sensitive probe of the extent of charge transfer. In the case of alkali doping, where charge is fully transferred from the metal atoms to C₆₀, the Raman frequency downshifts at a rate of ~7 cm⁻¹/charge. The relationship between the Raman shift of the A₈(2) mode and the formal valence is shown in the right panel of Fig. 18. The Raman shift for Ba₃C₆₀ is almost identical to that of K₆C₆₀ and the increase in Ba concentration causes a downshift of the A₈(2) mode at approximately the same rate as that for alkali-metal doping. This implies that the charge transfer from Ba to C₆₀ is also nearly full to a first approximation and the C₆₀ units in Ba₃C₆₀, Ba₄C₆₀ and Ba₆C₆₀ are close to hexa-, octa- and dodecavalent, respectively. Thus, Ba₄C₆₀ should have a partially filled t₁₈ band, while Ba₃C₆₀ and Ba₆C₆₀ should have full t₁₈ and t₁₈ bands, respectively.

Co-intercalation of alkaline-earth and alkali metals can lead to valence states which are not possible in simple binary compounds. An example is A₃Ba₃C₆₀ (A=K, Rb, Cs), which produces a nonavalent C₆₀⁹⁻ state [66, 67]. A₃Ba₃C₆₀ can be synthesized by reaction of alkali metals with preformed Ba₃C₆₀. It can be viewed as a solid solution of the two end compounds, Ba₆C₆₀ and K₆C₆₀, with which it is isostructural (space group Im₃). Importantly, this nonavalent phase shows superconductivity with maximum Tᶜ of 5.6 K.

Another ternary system is K₂Ba₄C₆₀ which is synthesized by reaction of excess potassium with preformed Ba₄C₆₀ [68]. Figure 19 shows the temperature dependence of the magnetic susceptibility of Ba₄C₆₀, K₃Ba₃C₆₀ and K₂Ba₄C₆₀ (Tᶜ=6.7 K, 5.6 K and 3.6 K, respectively). The diamagnetic signal of Ba₄C₆₀ disappears upon doping with K, with two onsets of superconductivity being displayed. The one at 5.6 K is attributable to K₃Ba₃C₆₀ impurity, while that at 3.6 K to K₂Ba₄C₆₀. The
volume fraction of this superconducting phase, which is isostructural with K₆C₆₀ and Ba₆C₆₀ (space group \textit{Im}₃, \(a=11.212\ \text{Å}\)) reaches \(\sim 14\%\), thereby implying bulk superconductivity.

Detailed understanding of the physical properties of superconducting alkaline-earth fullerides is still lacking. Among several interesting electronic properties, the A₃Ba₃C₆₀ systems show decreasing \(T_c\) with increasing lattice parameter (Fig. 20) [67] in sharp contrast to the case of A₃C₆₀, where \(T_c\) exhibits the opposite trend. Magnetic susceptibility measurements showed that the low \(T_c\) in A₃Ba₃C₆₀ reflects the low values of \(N(\varepsilon_F)\) (~5.7 and 4.1 states/eV/C₆₀ spin for K₃Ba₃C₆₀ and Rb₃Ba₃C₆₀, respectively), considerably smaller than that for K₃C₆₀ (13 states/eV/C₆₀ spin). Moreover, \(N(\varepsilon_F)\) for Rb₃Ba₃C₆₀ is smaller than that for K₃Ba₃C₆₀ despite its larger interfullerene spacing.

Possible explanations for this unusual behaviour have been offered by first-principles band structure calculations and synchrotron X-ray structural studies. The former revealed that, because of hybridisation between Ba and C orbitals, the rigid-band model is not appropriate for the description of the electronic properties and the calculated \(N(\varepsilon_F)\) for K₃Ba₃C₆₀ and Rb₃Ba₃C₆₀ are almost identical [69]. The structural analysis revealed positional disorder of the Ba²⁺ and K⁺ ions in the distorted tetrahedral sites of the \textit{bcc} structure and the existence of short Ba–C and K–C contacts, consistent with strong hybridisation between the K, Ba and the C₆₀ states [70]. It is important to notice that in K₅Ba₃C₆₀ there is a perfect matching between the size of K⁺ and Ba²⁺ ions, while in both the Rb⁺ and Cs⁺ analogues, there is a considerable mismatch, which leads to fundamental structural

**Fig. 19** Temperature dependence of the ZFC magnetic susceptibility of Ba₄C₆₀ (filled triangles), K₃Ba₃C₆₀ (filled circles) and K₂Ba₄C₆₀ (open circles)
and electronic consequences. For instance, the occupied site difference between Rb$^+$ and Cs$^+$ and divalent Ba$^{2+}$ should be even more pronounced than the one established for K$_3$Ba$_3$C$_{60}$, leading to increased local anisotropies and reduced $T_c$.

We now discuss the differences between alkali and alkaline-earth fullerides. First, superconductivity appears in the $t_{1u}$ and $t_{1g}$ bands for these systems, respectively, and $N(\varepsilon_F)$ of Ba-doped fullerides is smaller than that of alkali fullerides. Second, in the $t_{1g}$ band, once partial filling is achieved, the metallic state and superconductivity are simultaneously realised (Ba$_4$C$_{60}$, K$_3$Ba$_3$C$_{60}$, K$_2$Ba$_4$C$_{60}$, Ca$_5$C$_{60}$) albeit with lower $T_c$. In the alkali fullerides, on the other hand, the metallic state often competes with magnetic or non-magnetic insulating states, due to the Mott–Hubbard and Jahn–Teller instabilities. Superconductivity is found exclusively in the trivalent state and $T_c$ reaches values higher than 30 K. Thus an important difference of the electronic properties between alkali and alkaline-earth fullerides is the stability of the metallic state, which is quite robust in the $t_{1g}$ band and very fragile in the $t_{1u}$ band. Therefore, isostructural compounds, such as Ba$_4$C$_{60}$ and its alkali analogues A$_4$C$_{60}$, provide an important opportunity for a comparative study. Ba$_4$C$_{60}$ is a superconductor with $T_c$=6.7 K, while K$_4$C$_{60}$, Rb$_4$C$_{60}$ and Cs$_4$C$_{60}$ are all insulators.

A clue is obtained by careful examination of the crystal structures. It was found that in Ba$_4$C$_{60}$ there are several considerably small interatomic distances between Ba and C, one of which is 2.990(4) Å, almost identical to the sum of the ionic radius of Ba$^{2+}$ and the van der Waals radius of C. This short interatomic distance is strongly suggestive of strong hybridisation of Ba(5$d$) and C(2$p$) orbitals that causes bandwidth broadening [61]. The increase of the bandwidth suppresses several instabilities to the insulating states [71], which are often observed in the $t_{1u}$ compounds. This conjecture is also supported by first-principles calculations.
on Ba₆C₆₀, where hybridisation of Ba and C orbitals is found to play an important role in band broadening [72, 73]. Such orbital hybridisation implies that the ionic crystal model that assumes full charge transfer from metals to C₆₀ is not valid any more. However, considering the almost continuous Raman shift shown in the right panel of Fig. 18, full charge transfer provides a useful working model and hybridisation effects are not very dramatic. However, we stress that even weak hybridisation is sufficient to stabilise the metallic state.

3.2 Superconductivity in Rare-Earth Fullerides

The understanding of the structural, magnetic and electronic phase diagrams of rare-earth fullerides is still relatively poor, even though they display a plethora of interesting properties. Reaction of rare-earth metals with fullerenes requires high temperature because of their low vapour pressure. However, high-temperature reactions compete with the formation of rare-earth carbides. After carefully searching for the optimum reaction temperature and time, Özdas et al. reported superconductivity in Yb-doped fullerides with the chemical formula Yb₂.₇₅C₆₀ and T_c~6 K [74]. Soon thereafter, superconductivity at ~8 K was announced by Chen et al. [75] in Sm₂.₇₅C₆₀.

The crystal structure of Yb₂.₇₅C₆₀ is orthorhombic (space group Pcab) with the Yb cations occupying off-centred tetrahedral and octahedral interstitial sites [74]. One out of every eight tetrahedral sites is empty and long-range ordering of these tetrahedral vacancies results in a unit cell with dimensions twice as large as those of the commonly encountered fcc fulleride structures. The five symmetry-invariant C₆₀ molecules present in the unit cell (C₆₀(1) at (000), C₆₀(21) at (0,1/4,1/4), C₆₀(22) at (1/4,0,1/4), C₆₀(23) at (1/4,1/4,0) and C₆₀(3) at (1/2,1/2,1/2)) are rotated anticlockwise by 37.5° about local symmetry axes ([111], [11–1–], [1–11–], [–1–11] and [–1–11], respectively) (Fig. 21). X-ray photoemission experiments are consistent with the Yb ion being divalent, indicating that the average valence of C₆₀ is (C₆₀)⁵⁺ [76]. This leads to a partially filled t₁u band and metallic properties. However, in Ca₂.₇₅C₆₀, which is isostructural and isoelectronic to Yb₂.₇₅C₆₀, superconductivity is not observed. The electronic states of rare-earth fullerides deserve much additional careful investigation to achieve comprehensive understanding.

3.3 Intermediate Valence Behaviour and Lattice Response of Sm₂.₇₅C₆₀

As is evident from Sect. 3.2, the fullerene chemistry of the rare earths has not been explored in a systematic way due to the difficulties in devising reliable protocols for preparation of single-phase materials. Besides the early reports of Yb- and Sm-based superconducting phases, the exploration of the phase diagram of Eu–C₆₀ and –C₇₀ has led to the isolation of molecular ferromagnets [77–79], which exhibit metallic and negative magnetoresistive behaviour. Magnetic correlations develop either through direct exchange interactions between the lanthanides or through p- d, f interactions modulated by C₆₀.
We recently reported that when the structural properties of the Sm$_{2.75}$C$_{60}$ fulleride were probed by high-resolution synchrotron X-ray diffraction between 4.2 and 295 K, a giant isotropic negative thermal expansion in the temperature range 4.2 to 32 K at a rate of –400 ppm K$^{-1}$ was observed [80]. This is an order of magnitude higher than that observed in ternary metal oxides like ZrW$_2$O$_8$ [81]. The origin of the lattice collapse on heating is attributed to a quasi-continuous isosymmetric phase transformation which is driven by a temperature-induced valence transition of Sm from a nearly +2 oxidation state to an intermediate valence state of +(2+ε).

This effect is unprecedented in fullerene or other molecular systems and is reminiscent of the pressure-induced valence transitions encountered in mixed valence Kondo insulators like SmS [82]. In addition, no evidence was found in Sm$_{2.75}$C$_{60}$ for a transition to a superconducting state down to 2 K, in contrast to ref. [75] and in agreement with other explorations of the Sm–C$_{60}$ phase field [83].

Inspection of the synchrotron X-ray diffraction profiles of Sm$_{2.75}$C$_{60}$ readily reveals the appearance of superlattice peaks at low angles that index to the enlarged...
orthorhombic unit cell (space group $Pcab$) proposed for Yb$_{2.75}$C$_{60}$ [74]. However, a striking feature of the data is that the diffraction peaks at low temperatures continuously shift to higher angles on heating, implying an anomalous structural behaviour whereby the material rapidly contracts as the temperature increases above 4.2 K. The trend is reversed above 32 K and normal behaviour is restored with the lattice smoothly expanding on heating to 295 K. Besides the shifts in peak positions, no changes in peak intensities are apparent in the diffraction profiles throughout the whole temperature range, implying the absence of a phase transition to a structure with different crystal symmetry. Figure 22 shows the temperature evolution of the lattice constants and of the corresponding unit cell volume. Initially the lattice contracts slowly on heating above 4.2 K. Then the rate of contraction increases to $\frac{\text{dln}V}{\text{dT}} \approx -400$ ppm K$^{-1}$, resulting in an overall volume decrease of 0.84% between 4.2 and 32 K (Fig. 22 inset). The sign of the thermal expansivity then changes and the lattice expands on heating to 295 K at a rate of approximately $+20$ ppm K$^{-1}$, comparable to that typically encountered in other metal fulleride salts (e.g. for K$_3$Ba$_3$C$_{60}$, $\frac{\text{dln}V}{\text{dT}} \approx +30$ ppm K$^{-1}$) [70]. Despite this, the lattice dimensions of Sm$_{2.75}$C$_{60}$ at room temperature remain smaller than those at 4.2 K.

Refinement of the structure of Sm$_{2.75}$C$_{60}$ was performed by employing the structural model of Yb$_{2.75}$C$_{60}$ (Fig. 21). Stable refinements were quickly achieved, but even though agreement between observed and calculated profiles was very good, there were signs of systematic differences between model and experimen-

![Fig. 22](image_url)

Fig. 22 Temperature evolution of the orthorhombic lattice constants (left) and the unit cell volume (right) in Sm$_{2.75}$C$_{60}$. The inset shows an expanded view of the volume dependence on temperature in the range between 4.2 and 40 K.
tal intensities. We thus decided to allow partial occupation of the tetrahedral vacancy by Sm. The Rietveld refinement immediately improved significantly with the fraction of the Sm defect converging to ~25%. The obtained structural model is characterised by large displacements of the cations from the centres of the octahedral sites (~2.3 Å) and smaller displacements from the centres of the tetrahedral sites (~0.4 Å). However, the crystallographically distinct tetrahedral Sm ions in the unit cell do not have identical coordination environments, and careful examination of the metal–carbon distances revealed the presence of unphysically short contacts (2.52(3) Å) between Sm(3) located off the centre of the (3/8,3/8,3/8) tetrahedral hole and C_{60}(3) located at (1/2,1/2,1/2). Noting that the C_{60}(3) unit is surrounded by the maximum possible number of twelve near-neighbour Sm cations, we attempted to relieve the steric strain by exploring the suitability of alternative orientations. A satisfactory solution was found when C_{60}(3) was rotated anticlockwise by 37.5° about the local [111] (instead of [T1]) symmetry axis. This led to both an improved agreement between observed and calculated profiles and to physically meaningful shortest Sm(3)–C contacts (2.78(3) Å). The final average Sm–C distances are 2.91 and 2.94 Å for the tetrahedral and octahedral sites, respectively. The results of the final refinement at 5 K are shown in Fig. 23 (a=28.2025(2) Å, b=28.2397(2) Å, c=28.1632(2) Å).

The most prominent point arising from these results is the remarkable lattice response at low temperatures. The negative thermal expansion and quasi-con-
tinuous collapse of the structure of Sm$_{2.75}$C$_{60}$ on heating are not accompanied by a change in crystal symmetry and the full space group is preserved. The origin of negative thermal expansion behaviour over broad temperature ranges in oxides like ZrW$_2$O$_8$ [81] has been associated with the presence of low-energy highly anharmonic transverse thermal vibrations, which tend to contract the lattice. Although anomalies in the low-energy phonon spectrum may well occur in Sm$_{2.75}$C$_{60}$ through the transition, possibly associated with strong coupling between Sm and C$_{60}$ motion, we favour an explanation of the effect based on the fragility of the valence states of Sm and its tendency to exhibit intermediate valence characteristics. Firstly we recall that the unit cell size of metal fullerides is sensitively controlled by the size of the ions residing in the small tetrahedral interstices. In Sm$_{2.75}$C$_{60}$, the tetrahedral hole has a radius of 1.12 Å, straddling the values of the ionic radii of Sm$^{2+}$ (1.14 Å) and Sm$^{3+}$ (0.96 Å). A valence transition of Sm from +2 towards an intermediate value of +$(2+\epsilon)$ with smaller ionic size, induced on heating, will thus have a profound effect on the lattice size and is consistent with the observed dramatic volume decrease.

Such mixed-valence behaviour is well documented in rare-earth compounds like the samarium monochalcogenides. For instance, SmS (NaCl-type structure) undergoes an abrupt (first-order) catastrophic transition from a semiconducting black phase to a metallic gold one at 0.65 GPa at ambient temperature [82]. In contrast to SmS, the transformation is continuous in SmSe and occurs over a broad pressure range (0–5 GPa). In both cases, the transitions are isosymmetric and are characterised by a large volume collapse consistent with the conversion of Sm$^{2+}$ to Sm$^{3+}$. The rare-earth metal valence is typically derived by lattice parameter measurements, by magnetic susceptibility or by spectroscopic methods. A charge (valence) fluctuation model (+$2(4f^{6}5d^0)\rightarrow+3(4f^{5}5d^1)$) has been employed to describe the physics of these systems with the valence transition controlled by the Kondo temperature, which reflects the strength of the hybridisation between the 4$f$ and the 5$d$ conduction electrons. The transition pressure can be successfully lowered by alloying SmS with trivalent rare-earth metals, Ln, to give Sm$_{1-x}$Ln$_{x}$S compositions. In such cases and for selected values of the dopant level $x$, the collapsed intermediate valence (Sm$^{(2+\epsilon)}$) phases can be stabilised at ambient pressure whereby upon cooling they exhibit either continuous or discontinuous valence transitions accompanied by expansion of the lattice dimensions [84], much like what is observed here for Sm$_{2.75}$C$_{60}$.

Figure 24 shows the results of magnetic measurements for Sm$_{2.75}$C$_{60}$. The diagram also includes the calculated magnetic susceptibilities of the free Sm$^{2+}$ and Sm$^{3+}$ ions. For Sm$^{2+}$ ($4f^{6}, 7F_0$), the Curie contribution of the ground state to the magnetic susceptibility is explicitly zero and there is only a van Vleck term arising through the mixing of the $J=0$ ground and the $J=1$ excited state (energy separation=420 K). The susceptibility of Sm$^{3+}$ ($4f^{5}, 6H_{5/2}$) is obtained by summing the corresponding Curie and van Vleck (energy separation between $J=5/2$ ground and $J=7/2$ excited state=348 K) contributions. The room-temperature value of the magnetic susceptibility of Sm$_{2.75}$C$_{60}$ ($\chi_{RT}=3.75\times10^{-3}$ emu/mol Sm) straddles those calculated for the free Sm$^{2+}$ and Sm$^{3+}$ ions. At sufficiently high temperatures in intermediate valence compounds, the measuring scale is faster than the fluctuation rate between the two valence configurations and the magnetic suscepti-
bility is expected to be a linear combination of the Sm\(^{2+}\) and Sm\(^{3+}\) contributions, 
\[ \chi_{\text{RT}} = (1 - \varepsilon)\chi(\text{Sm}^{2+}) + \varepsilon \chi(\text{Sm}^{3+}) \].
The room-temperature susceptibility of Sm\(_{2.75}\)C\(_{60}\) then provides an estimate of the average Sm valence as approximately equal to +2.3. We also include in Fig. 24 the temperature dependence of the calculated average susceptibility assuming 70 and 30% contributions from Sm\(^{2+}\) and Sm\(^{3+}\), respectively. This follows the experimental data very well down to about 40 K, just above the onset of the valence transition, and then diverges significantly.

3.4 Bonding Nature and Structural Properties of Sm\(_{2.78}\)C\(_{70}\)

As evidenced by the electronic properties of alkaline-earth and rare-earth fullerenes, the role of intercalated metals considerably differs from that in alkali fullerenes, where charge transfer from cations to fullerenes is generally complete and the interaction between the cations and fullerene anions is purely ionic. In contrast, physical properties, such as superconductivity and giant magnetoresistance [77] in alkaline-earth and rare-earth fullerenes, suggest a different bonding nature from that in alkali fullerenes. For instance, the role of Ba–C hybridisation was particularly exemplified in the careful structural analysis of Ba\(_4\)C\(_{60}\) [61], as discussed in Sect. 3.1. In addition, direct evidence of orbital hybridisation between rare-earth ions and carbon atoms was provided by the electron distribution map of Sm\(_{2.78}\)C\(_{70}\), which was derived by a combined analysis of the maximum entropy
method (MEM) and Rietveld refinement of synchrotron X-ray powder diffraction data [85]. The strong orbital hybridisation also causes a unique pressure-induced structural transition in Sm$_{2.78}$C$_{70}$.

In conventional Rietveld refinements, a structural model based on the arrangement of atoms in the unit cell is generally used. However, the imaging ability of MEM in the MEM/Rietveld method enables one to visualise more detailed features like the bonding electron distribution associated with hybridised orbitals [86]. Sm$_3$C$_{70}$ was found to adopt a pseudo-monoclinic cell with lattice dimensions $14.860(1) \times 10.091(2) \times 10.918(2)$ Å$^3$, $\beta=96.173(5)^\circ$ (space group $P1$). The MEM charge density shown in Fig. 25 reveals a unique bonding nature with evidence of not only the C–C covalent bonding features in C$_{70}$, but also of an overlapping of the charge density between one of the tetrahedral Sm ions and C$_{70}$. Interestingly, only one Sm ion displays a significant overlapping electron distribution with C, which is taken as the signature of Sm–C bond covalency. Such a strong overlapping electron distribution between metal ions and carbon atoms has never been observed in earlier studies of alkali fullerides [87], which displayed the typical behaviour of ionic crystals. The charge density value at the midpoint of the Sm–C bond is equal to 0.6 [eÅ$^{-3}$], which is close to those of interatomic bonds in Si crystals and Mn–O bonds in manganites [88]. Therefore, it can be concluded that the essential structure of Sm$_{2.78}$C$_{70}$ comprises a C$_{70}$ dimer covalently bridged by Sm.

This novel dimer structure provides a new insight into fullerene solids, which have been known to form van der Waals or ionic crystals. For instance, in most fullerene intercalation compounds, molecules start to rotate near room temperature, accompanied by orientational disorder phase transitions, due to the weak intermolecular interactions. Even polymeric fullerenes revert to monomers at ~100–200 °C. A high-temperature X-ray diffraction experiment on Sm$_{2.78}$C$_{70}$, on the other hand, shows that the diffraction pattern is unchanged up to 550 °C, indicating that the dimer structure is maintained at least to 550 °C. This remarkable stability of the dimer implies that the Sm–C bond is much stronger than conventional interfullerene bonds, in agreement with the observed charge density.

The dimer structure in Sm$_{2.78}$C$_{70}$ also causes a unique structural phase transition under pressure at ~1.5 GPa [89]. The volume compressibility of the

![Fig. 25 Equicontour (0.6 eÅ$^{-3}$) map of the MEM charge density for Sm$_{2.78}$C$_{70}$](image-url)
Sm$_{2.78}$C$_{70}$ dimer phase at low pressures, $\kappa=0.038(1)$ GPa$^{-1}$, is comparable to that of fcc fullerides. In sharp contrast, $\kappa$ is substantially reduced to 0.020(1) GPa$^{-1}$ for the high-pressure phase, suggesting much tighter crystal packing and/or stronger interactions between dopant cations and fulleride anions above 1.5 GPa. The cross section of the charge density map obtained by the MEM/Rietveld method for the high-pressure phase of Sm$_{2.78}$C$_{70}$ is shown in Fig. 26 together with that at ambient pressure. This allows us to conclude that the phase transition is driven by the simultaneous movement of rare-earth ions and C$_{70}$ molecules, due to steric crowding at high pressure. At ambient pressure, the tetrahedral ions are shifted from the site centre as they participate in the formation of Sm–C bonds. By application of hydrostatic pressure, the metal ions are driven back to the site centre, possibly causing the collapse of the dimer structure and reorientation of C$_{70}$. The high-pressure state can be regarded as a new type of polymeric fullerene structure with a 3D bonding network, consistent with the measured small compressibility.

4 Conclusions

Work on the condensed phases of fullerenes and their derivatives continues to lead to unexpected results whose significance extends to other areas of solid-state chemistry and physics. Unlike in other superconducting materials, the key ingredients in the mechanism of superconductivity, namely the electron–phonon coupling strength (an intramolecular property) and the density-of-states at the Fermi level (an intermolecular property) are decoupled. This has allowed the exploration of a large parameter space in a systematic manner by structurally modulating $N(\varepsilon_F)$, while keeping $V$ essentially fixed. The metal-intercalated fullerides are also archetypal examples of strongly correlated electron systems. Their unique electronic and crystal structures allow them to display previously
unsuspected aspects of the important Mott–Hubbard model. This has generic significance, as most high-$T_c$ superconductors are located precisely at such MI boundaries and there are clear recent theoretical predictions [90] that the strong correlations may provide a mechanism for further enhancement of fulleride superconductivity to above 40 K. Finally, the emerging results on the properties of rare-earth fullereides open the way for the synthesis and study of new families of molecular-based strongly correlated Kondo and heavy fermion systems with strong coupling between the charge, lattice and spin degrees of freedom. As electronically active anion solids, the rare-earth fullerides will have properties intrinsically unattainable in comparable rare-earth chalcogenides with closed-shell anions, and entirely novel phenomena can be expected.

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5
References

Structural and Electronic Properties of Selected Fulleride Salts

50. Margadonna S, Prassides K unpublished results
Abstract  Many unique properties of C_{60}-based materials stem from the fact that purely molecular properties survive in the solid state, adding a level of complexity to their description. As the molecules are only weakly bonded by Van der Waals interactions, the overlap between their electronic wave functions is small and narrow bands are formed. Because of the narrowness of these bands (typically 0.5 eV), these materials are expected to be strongly correlated systems. The Coulomb repulsion between electrons is indeed estimated to be of the order of 1 eV, much larger than the bandwidth, so that the equilibrium between localizing electrons to avoid the energy cost of a double occupancy of one site and delocalizing electrons to gain kinetic energy is uncertain. These strong correlations probably play a role in the various electronic properties observed as a function of the filling of the lowest unoccupied molecular orbital by electrons from alkali ions, such as superconductivity in A_3C_{60} (and only A_3C_{60}), the half-filled case, but also insulating phases for A_{4}C_{60}, which cannot be explained by a simple band picture. Equivalently, the strong Coulomb repulsion will tend to increase the average time spent by one electron on a given molecule, because hopping to the next ball might not be favorable, and during that time, “molecular physics” is relevant and will therefore be intimately mixed into the electronic properties of the solid. This suggests that molecular features that would be typically washed out in simple metals may survive here.

One interesting example is the Jahn–Teller effect, which can lead to a spontaneous distortion of the C_{60} molecule. It turns out to be particularly important in fullerenes because of the strong electron–phonon coupling and the icosahedral symmetry of the C_{60} molecule. This high symmetry leads to large degeneracies in electronic and phonon levels which are at the origin of the Jahn–Teller effect. Although it is a purely molecular property, we will show that it has important consequences in the solid state, as it is very sensitive to the number of electrons occupying a C_{60} ball. This number will change with time if hopping takes place, leading to an interesting competition between delocalization of electrons and stabilization of Jahn–Teller distortion. Unfortunately, the distortions themselves are very small and possibly dynamic, so that they are hardly directly detectable, leading to a lack of experimental basis in the analysis of this effect.

The purpose of this chapter is to introduce the basic notions related to the Jahn–Teller effect in fullerenes and to examine how it affects the properties of these solids, mainly in the case of alkali-doped fullerenes. A brief survey of the theoretical notions important to understand this effect will be given in the first part. As illustration, we will present examples of a few cases where clear manifestations of Jahn–Teller-related effects have been observed, mostly chosen in diluted salts where the molecules can be considered as isolated. We will then focus our attention on alkali-doped fullerenes, and particularly the relationship between metallic and insulating phases. We will argue that the different stability of the Jahn–Teller distortion for an odd or even charge of a C_{60} ball considerably affects the behavior of these systems. This will be developed through the study of three different situations encountered in these systems. The second part deals with compounds where static distortions are created as defects within a metallic phase. We will show that for these distortions the electrons are localized in pairs, even though the stoichiometry corresponds to an odd number of electrons per C_{60}. In the third part, we will argue that the insulating nature of most even stoichiometries can be understood.
by strong electronic correlations enhanced by the Jahn–Teller distortion. In the fourth part, we will generalize the formation of electronic pairs via Jahn–Teller distortions in metals to the dynamic case. Finally, we will conclude that altogether, this set of data strongly supports the idea that Jahn–Teller-related interactions are a major source of electronic correlations for these solids.

Keywords Jahn–Teller effect · Superconductivity · Disproportionation · Nuclear magnetic resonance

1 Introduction: Jahn–Teller Effect in Fullerides

1.1 The Jahn–Teller Effect

The Jahn–Teller (JT) effect occurs in the presence of degenerate electronic states. A spontaneous distortion of the lattice (or here of the C\textsubscript{60} molecule) would lift the degeneracy between these states, if it reduces the symmetry at the origin of the degeneracy. If these levels are only partially occupied, the electrons occupy the...
low-lying states, causing the total electronic energy to decrease. A theorem due to Jahn and Teller states that, except for linear molecules, this will compensate the energy cost associated with the deformation of the lattice, so that a distortion is indeed favorable, in much the same way that a charge density wave (CDW) instability can be stabilized in an itinerant system.

To understand the role of the JT effect in $C_{60}$-based materials, we would like to calculate the modification of the shape of the molecule, the magnitude of the distortion, the splitting it induces among the electronic levels, and the gain of energy associated with the distortion. Other important features such as the dynamic or static nature of the distortion will be considered later.

Let us first solve the simpler problem of a doubly degenerate electronic level in interaction with a single mode of vibration, to introduce the important parameters (such a system was considered by O’Brien et al. [1]). The Hamiltonian should involve the kinetic energy for the electrons and for the ions, the potential ionic energy, and the coupling between electrons and ions. Within the adiabatic approximation, the fast motion of the electrons can be decoupled from the slow motion of the ions. The electronic energies are calculated first and will be considered in the following as a reference. The electron–phonon coupling acts as a perturbation shifting these electronic levels. To first order, this coupling is assumed to be linear and the respective symmetries of the electronic and phonon wave functions fix its form; in the simple case we consider, there is only one possible form. By calling $X$ the coordinate associated with the phonon mode, we then obtain:

$$H = \frac{1}{2} M \frac{d^2}{dX^2} - \frac{1}{2} KX^2 + g \begin{bmatrix} -X & 0 \\ 0 & X \end{bmatrix}$$

where $M$ is the ionic mass, and $K$ and $g$ are the respective strengths of the oscillator and of the electron–phonon coupling. The matrix operates within the pair of electronic states as basis. Although we will consider spin degeneracy, it does not appear explicitly here as the coupling is independent of spin. In a second quantization language, $X$ will be expressed in terms of the creation and annihilation operators for phonons $b$ and $b^+$.

$$b = \frac{1}{\sqrt{2}} \left( \sqrt{\frac{M\omega_b}{\hbar}} X + i \frac{P}{\sqrt{M\omega_b\hbar}} \right) \text{ so that } X \propto \left( b + b^+ \right)$$

$\omega_b$ being the phonon frequency ($\sqrt{K/M}$ in a classical picture). The quantum equivalent of Hamiltonian Eq. 1 is then

$$H = \hbar \omega_b \left( b^+ b + \frac{1}{2} \right) + g \left( c_1^+ c_2^+ \right) \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} \left( b + b^+ \right)$$

The great simplification with this model is that the coupling does not mix the two electronic states, so that diagonalization is straightforward.
In the adiabatic approximation, the kinetic energy of the ions is neglected, and the distortion will be considered as “frozen” to a value \( \langle X \rangle \) (equivalently \( \langle b \rangle \)) that minimizes the other terms in the energy. This gives a simple parabolic form for the energy represented in Fig. 1:

\[
E (\langle X \rangle) = \frac{1}{2} K \langle X \rangle^2 - g \langle X \rangle n_1 + g \langle X \rangle n_2
\]

where \( n_1 \) and \( n_2 \) are the occupation numbers of the two electronic states. The strength of the coupling determines the equilibrium position:

\[
\langle X \rangle = \frac{g}{K} (n_1 + n_2)
\]

Logically, this tells us that there will be no distortion if the states are completely occupied or completely empty, because there cannot be an associated gain of electronic energy. Likewise, the size of the distortion increases with double occupancy. The shifts of the electronic levels introduced by the distortion (i.e., \( g \langle X \rangle \)) are also shown in Fig. 1 for each case. For three electrons (not shown), the distortion would be identical as for one.

This simple example already allows one to get a feeling of the importance of the different parameters: if the coupling is very strong the energy minima will be well separated and the electronic wave functions will be localized at the

---

**Fig. 1** Scheme of the potential energy seen by electrons for the simple case where two electronic levels interact with a single mode of vibration (see Eq. 1). The top part of the figure sketches the potential energy seen by the electrons while the bottom part sketches the shift induced by the Jahn–Teller distortion on the electronic levels. \( E_{JT} \) is the energy gained by the JTD.
minimum of a well. This case is the one where this “classical” treatment, where all quantum fluctuations around the equilibrium are neglected, is appropriate. As the coupling gets weaker, there will be an increasing overlap between the distorted states and electrons could tunnel from one well to the other. The distortion will likely be dynamic, its size reduced, and the original symmetry of the molecule dynamically restored. Also, one can expect that if the spacing $\omega_0$ of the quantified oscillator levels in the well (and the associated zero-point motion) is sizable compared to $E_{JT}$, the behavior of the system could be significantly modified. This condition is related to the weak coupling limit. It will be also be more sensitive to the population of excited states with temperature.

For C$_{60}$, the coupling is in fact presumably in an intermediate coupling regime, so that all these effects should be taken into account and JT distortions could manifest themselves in a variety of ways. However, the previous classical treatment is very useful as a starting basis to get an intuitive idea of the situation and will be introduced now. The principle of the calculation is not fundamentally different than in the previous simple model, although symmetry considerations become more complicated as the number of modes involved increases, as well as their degeneracy.

The lowest unoccupied molecular level of C$_{60}$ is threefold degenerate (not including spin degeneracy) and has a t$_{1u}$ symmetry. It arises from the L=5 level of a spherical shell model of the molecule split by the icosahedral symmetry of the actual ionic potential. For many purposes, this set of orbitals can be considered to play, for the molecule, a role similar to that of the set of $p_x$, $p_y$, and $p_z$ orbitals for a carbon atom. For the vibrational part, a molecule of 60 atoms will have $3 \times 60 = 180$ vibrational modes (–6 for translational modes). Fortunately, for symmetry reasons, only a few of them can couple to the t$_{1u}$ levels, namely those contained in the symmetry product $(t_{1u} \ast t_{1u})_s$, in fact two A$_g$ modes and eight H$_g$ modes. They correspond to high-frequency (from 34 to 195 meV) vibrations of the molecule. As far as the JT effect is concerned, it turns out that the A$_g$ do not lift the degeneracy because they are highly symmetric. We can therefore focus our interest on the eight H$_g$ modes, each of which is fivefold degenerate.

The problem of a triply degenerate electronic level interacting with a mode of vibration of fivefold degeneracy was actually considered long ago in different systems [2, 3]. The electron–phonon coupling will now be described by:

$$H_{el-ph} = \sum_{\nu} g_{\nu} \sum_{m} \sum_{i,j} V_{ij}^{(m)} c_i^+ c_j (b_{\nu,m} + b_{\nu,m}^*)$$

where the sum $\nu$ runs over the eight H$_g$ modes, the sum $m$ over their fivefold degeneracy, and the sum $i,j$ over the three t$_{1u}$ electronic levels. $V_{ij}$ are matrices describing the coupling to the H$_g$ modes in accordance with the symmetry of these states [2–5].

Auerbach et al. have carried out this calculation in detail [4]. Treating the phonon modes as “frozen”, they have found two kinds of distortion depending on the number of electrons on the C$_{60}$, which are represented in Fig. 2. A unimodal distortion leaves two of the electronic levels degenerate, because of its axial symmetry. The single level will be at lower energy if the molecule is elongated along one axis and at higher energy if it is squeezed. For one or
two electrons, the uniaxial elongation is favorable to minimize the energy of the electron(s) in the lowest single level. With no on-site Coulomb repulsion and everything else being equal, the distortion will be stronger with two electrons, since the gain of energy is larger. A uniaxial squeezing will be preferred for four or five electrons for similar reasons. Finally, for three electrons, a new bimodal distortion, which eliminates all the degeneracies is preferred (see Fig. 2). The resulting ordering of the $t_{1u}$ levels as a function of the C$_{60}$ charge are sketched in Fig. 3. Note that this picture presents a very simplified view of the situation, where all correlations between electrons are neglected. These two interactions have in fact the same order of magnitude and should both be considered to find the true ground state.

For the uniaxial distortion, total-energy minimization calculations [6] show that the major distortions occur near an “equator” of the C$_{60}$ molecule. The bonds perpendicular to the equatorial plane are stretched and those contained in the equatorial plane are compressed. The displacement of each atom is only, at most, 0.05 Å for about 20 atoms located near the equator.

![Fig. 2a, b](image)

Fig. 2a, b  Polar representation of the Jahn–Teller distortion of the C$_{60}$ molecule obtained with a strong coupling calculation. a) Unimodal distortion occurring for $n=1, 2, 4, 5$. b) Bimodal distortion for $n=3$. (After [4])

![Fig. 3](image)

Fig. 3  Representation of the shift of the electronic levels induced by the Jahn–Teller distortion as a function of the C$_{60}$ charge. Here, electrons are treated as noninteracting to illustrate the role of JTD only. This alone would not be a realistic description of fullerides, where electronic correlations are on the contrary very strong.
Such calculations are based on a linearly coupled JT system, and the location of the different minima of the potential energy still have a spherical distribution. Only when the next order JT effect is included does this spherical symmetry become warped and a distortion with either D_{5d} or D_{3d} symmetry give the minimum energy [6]. These higher order effects—arising for example from the inclusion of molecular levels of higher energy or from anharmonicity of the phonon modes—are not very significant in C_{60}, where the t_{1u} level is well separated from the other and the C–C bonds are quite stiff [7]. Indeed, detailed Hartree–Fock calculations have shown that the energy gains by going from the icosahedral symmetry I_{h} to D_{5d}, D_{3d}, or D_{2h} via static JT distortion for a C_{60} are within 1% [8]. In these different cases, the JT distortion occurs by ellipsoidal elongation along the C_{5}, C_{3}, or C_{2} axes, with the singly occupied orbitals located mainly in the equator. However, it should be kept in mind that there are slightly different types of distortion, nearly degenerate in energy, between which a molecule could oscillate. Alternatively, in the solid state, crystal field effects could become important and might stabilize one of them.

1.2 Structural Evidence of Jahn–Teller Distortions

The smallness of the C atom displacements expected theoretically as a result of the Jahn–Teller distortion (JTD) makes it obvious that the direct detection of JTD will be very challenging. As the coupling between molecules in a metallic phase will add new degrees of freedom and considerably complicate the problem, the study of a “simple” model system where the C_{60}^{2–} could be considered as nearly isolated is highly desirable. Such phases have been obtained in C_{60} salts, principally with C_{60}^{2–} and C_{60}^{4–}, where large counter anions lead to a distance between C_{60} centers of typically 12.6 Å compared to 10 Å in alkali fullerides (for a review on C_{60} salts, see ref. [9]).

One of the clearest cases is obtained for a salt of bis(triphenylphosphine)-iminium ion (PPN+) and C_{60}^{2–}. It was found [10] that the distorted fullerene molecule exhibits, as can be seen in Fig. 4, an axial elongation with a rhombic squash, in good agreement with the type of JTD described previously. While in the ideal icosahedral structure the distances of the carbon atoms from the center of the molecule are exactly equal, in the distorted structure there is a spread of ±0.04 Å around the mean value of 3.542 Å.

In this case, a detailed structural investigation was possible because of the high degree of orientational order. It is believed that this order results from an electrostatic interaction between the electron-rich hexagon of the C_{60} and the dipole formed by the C–H bonds of the solvent placed near the equator of the C_{60} molecule. Therefore, there remains a possibility that such interactions also affect the distortion, which might not represent the purely intrinsic JTD.

Another case, this time for C_{60}^{2–}, was reported by Wan et al. [11] for [Ni-(C_{2}Me_{5})^{2+}][C_{60}]CS_{2}. As shown in Fig. 5, they have also found a distortion located around the equator of the molecule, although, contrary to theoretical expectation, the molecule is this time squashed and not elongated along one axis. The absolute value of the distortion is slightly larger than in the previous case (±0.05 Å). In this
Fig. 4 Size and color visualization of the distortion of $\text{C}_{60}^{2-}$ in [PPN$^+$][C$_{60}^{2-}$]. Carbon atoms at a distance greater (or smaller) than 0.007 Å from the mean center-to-C-atom distance are white (or dark). (From [10])
structure, the C$_{60}$ is axially sandwiched between two cations, presenting a five-membered C ring very close to one C$_{60}$ pentagon face. Here again, this interaction might play a role in the distortion.

Overall, such studies support the tendency for C$_{60}$ molecules to undergo JTD according to the shapes predicted in the calculations and with very small amplitudes. It seems possible that an interaction with the solvent stabilizes a static distortion in the reported cases. The true nature of the JTD for a free molecule being intrinsically dynamic, this could explain why JTD have remained elusive in many other cases.

1.3 Static vs Dynamic Distortions

As already discussed, the important parameters to determine whether the distortion is static or dynamic will be (i) the overlap between wave functions in different potential wells, mainly depending on the strength of electron–phonon coupling $g$ and (ii) the importance of quantum fluctuations measured by the size of $\omega_0$ compared to $E_{JT}$ (a condition related to the previous one). In addition, a strong crystal field could trap the molecular distortion in one particular well by breaking the symmetry between the three different orbitals. A particular collective distortion could also be adopted as a result of the introduction of a hopping term between the molecules, if it reduces the kinetic energy of the band. This will be discussed in more detail in the last paragraph of this section.

Because the temperature of superconductivity observed in A$_3$C$_{60}$ fullerides is high, people sometimes assume that the electron–phonon coupling must be very strong. It is actually not so; the unusually high frequencies of the phonon modes likely to be involved in superconductivity (precisely the H$_g$ modes that are also JT active) help to enhance $T_c$, but the coupling to these modes is only moderately strong, partly because the coupling to very high frequency modes is not so

Fig. 5 Stereoscopic visualization of the distortion of C$_{60}$. C-atom-to-center distances longer (or shorter) by 0.01 Å compared to the mean value are represented in black (or white). (From [11])
efficient ($g$ is inversely proportional to the phonon frequency). A precise value for this coupling is difficult to obtain (for references and a discussion of this problem, see the review by Gunnarsson [12]). There are several sets of calculations estimating the $H_g$ contribution to the dimensionless parameter $\lambda = \sum_{\nu,\mu} N(0)g^2/\hbar\omega$, as about 0.4 despite some differences in details [12]. Experimentally, the coupling has been determined for a few modes by the width of the Raman scattering or neutron spectra, or by the intensity of the phonon satellites in the photoemission spectrum of $C_{60}^-$ in the gas phase. The uncertainty of these values is rather large, but consistent with such a value for the coupling. Together with the fact that these large phonon frequencies imply large zero-point energies, this situation requires a quantum description.

Such corrections were discussed by Auerbach et al. [4]. Assuming weak coupling, they have found in a perturbative calculation that quantum corrections are quantitatively important to calculate the energy of the different levels (they can renormalize the results by a factor as large as 2.5). On the other hand, Gunnarsson performed a calculation [5] including all the modes without assuming weak coupling and obtained values intermediate between the weak and strong coupling cases.

1.3.1

$C_{60}$-tetraphenylphosphonium Halide

Historically, the first experimental evidence of the JT effect was observed by ESR by the splitting of the Lande factor ($g$-tensor) in 1952 on magnetically diluted $Cu^{2+}$ salts. Indeed this factor is very sensitive to even small deviation from the cubic symmetry, as will be the case for a static JTD. However, in many cases, such effects could be hidden for $C_{60}$-based materials by broad linewidths arising from strong electron-spin interactions. It is essential to work with well-separated $C_{60}^-$ ions for this effect to be detectable.

In $[A+(C_6H_5)_4]_2C_{60}^- B^-$ (A stands for As or P, and B for I or Cl), $C_{60}^-$ ions are surrounded by eight Ph$_4P^+$ cations. An advantage of this system is that single crystals can be grown by electrocrystallization. At room temperature, the structure is tetragonal with space group $I4/m$ with merohedral disorder between two $C_{60}^-$ orientations.

ESR detects a splitting of the Lande factor below 140 K, as is represented in Fig. 6 at $T=40$ K, consistent with a static JTD [13]. The largest value of the $g$-tensor ($g_{zz}$) was not found parallel to the tetragonal $c$-axis, suggesting that the direction of elongation is dictated by molecular symmetry and not crystal field effects. The two other values of the $g$-tensor are similar, as expected for axial symmetry, but not strictly equal, leading Bietsch et al. [13] to conclude in favor of a $D_{2h}$ distortion.

On the other hand, far infrared transmission measurements [14] have found doublet splitting of the $F1u(1)$ and $F1u(2)$ modes and activation of silent odd modes already at room temperature. Because of the rapid timescale of the IR measurements, this suggests that there is a dynamic JTD at room temperature which becomes static below 140 K. Interestingly, a detailed x-ray diffraction study of this material [15] has evidenced an orientational transition at about the
same temperature. It appears likely that the orientational ordering transition induces stabilization of a JTD of a given symmetry along a specific molecular axis, because the crystal-field symmetry is indeed lowered from 4/m to 2/m at the transition. This is an example of how molecular and bulk properties both contribute to the finding of the most stable situation.

1.4 Multiplet Structure

Even when a distortion cannot be directly detected, it can have deep consequences for the electronic properties of these materials. For example, there is a clear-cut competition between JT effect and the molecular Coulomb correlations. Hund’s rules would tend to form a high-spin state that minimizes repulsion between electrons, while JT-split electronic levels imply a low-spin ground state.

In the absence of JTD, one could already place electrons on C$_{60}$ in a number of ways, provided their spin and orbital moment combine in an antisymmetric wave function. Two electrons could occupy the same orbital (singlet $^1A_g$) or two different orbitals in a triplet state ($^3T_1_g$) or singlet ($^1H_g$ which has a nonzero orbital moment contrary to $^1A_g$). The relative energy of these different states will be given by the value of the Coulomb repulsion sensed in the different configurations, which mainly depends on the exchange integral $J$. For fullerides, this is only a small fraction (about 50 meV) of the total Coulomb repulsion sensed by two electrons on the same site (about 1 eV), but this will give rise to a substructure of the $t_{1u}$ levels in molecular terms typically of the energy scale of the JT splittings. The effect of a JTD should then be considered on each of these different configurations rather than on the simple electronic level of Fig. 3.

As a matter of fact, the analysis of free C$_{60}^{-}$ ions clearly reveals a low spin state for C$_{60}^-$ (S=1/2), C$_{60}^{2-}$ (S=0), C$_{60}^{3-}$ (S=1/2) indicating a violation of Hund’s rules,
Fig. 7  a Magnetic moment versus temperature for a C$_{60}^-$ fulleride salt ([PPN][C$_{60}$].PhCN.THF (solid symbol)) and for a C$_{60}^3^-$ fulleride salt ([PPN]$_3$[C$_{60}$].2CH$_3$CN (open symbol)). b A representative ESR spectrum of C$_{60}^2^-$ showing the three typical signals. The spectrum was recorded at 85 K for the [PPN$^+$] salt in benzonitrile. (From [9])
which points indirectly but very strongly to the importance of JT interactions. This was established by magnetic susceptibility measurements and ESR (for a review, see [9]). There has been some controversy regarding the interpretation of these data over the years (for example because of the frequent presence of a narrow signal in ESR, which is now recognized as extrinsic), but the qualitative picture has now emerged. Figure 7a shows the temperature dependence of the magnetic moment for $C_{60}^-$ and $C_{60}^{2-}$ in similar solvents. They are nearly identical and correspond to a spin 1/2. Figure 7b represents a typical ESR spectrum for a $C_{60}^{2-}$ ion. Three different lines can be distinguished: the central line is probably of extrinsic origin; the two other lines correspond to two different triplet states—one is already present at low temperatures (4 K) and the other one, appearing only around room temperature, is an excited state. On the other hand, the value of susceptibility implies that at least half of the molecules are in a singlet state at low temperature, which means a singlet and a triplet state are almost degenerate in this case.

The prediction of the ordering between singlet and triplet states is delicate as there are many competing interactions on similar energy scales. For example, it can be anticipated that a JTD that squeezes the molecule instead of elongating it will correspond to a triplet for $C_{60}^{2-}$, as it leaves two degenerate low-lying states. The gain of energy lost for the JTD will be partially compensated by the gain of energy associated with the smaller Coulomb repulsion in the triplet state, so the two states are finally close in energy. For a $C_{60}^{4-}$, the singlet is calculated to be the lowest state but only by about 100 meV. Note that the ESR results prove that there are a variety of excited states accessible within thermal energies.

1.5 Pair Energies and Mediated Effective Electronic Interactions

Up to now, we have mostly considered isolated molecules and studied how the distortion changes with the $C_{60}$ charge. When the molecules form a solid, so that there is a (small) overlap between the electronic orbitals, there will be competition between the JT energy and the delocalization energy of the electrons. This creates a rich physics that we will review in this chapter.

The first consequence of JT interaction one can think of is that it introduces a dissymmetry with respect to hopping. In a lattice of molecules with an average number of $n$ electrons per $C_{60}$, it is obvious from Fig. 3 that the gain of energy will be larger if $n$ is even rather than odd. Therefore, if one electron hops to the next ball leaving a $C_{60}^{(n-1)-}$ and a $C_{60}^{(n+1)-}$, the new states will be stabilized by JTD ($n$ odd) or destabilized ($n$ even). This suggests that JTD could indirectly favor hopping or localization depending on the parity of $n$. To study this quantitatively, one can calculate the pair energies defined by:

$$U_{\text{eff}} = E(n+1) + E(n-1) - 2E(n)$$

Such pair energies have been calculated by various groups [5, 7, 16] and the variation of $U_{\text{eff}}$ with $n$ is represented qualitatively in Fig. 8. The maximum amplitude of $U_{\text{eff}}$ is about 100 meV.
This contribution will add to the Coulomb repulsion and modulate its effective value. The sign of the contribution alternates between even and odd stoichiometries, meaning that the JTD induces attractive correlations in odd-electron systems and repulsive correlations in even-electron systems. Compared to the magnitude of $U=1\ \text{eV}$, this could seem negligible at first, but these solids are very close to the Mott metal–insulator transition and even a small change in the value of the ratio $U/W$ could be decisive in triggering a transition.

Let us mention that there is a more subtle effect introduced by a dynamical JT effect in the form of a new degree of freedom, the “berry phase”. This can lead to interference effects, which would constrain the tunneling of charge carriers in a lattice of molecules. This can renormalize the electron–electron interaction and it has been proposed that it could favor electronic pairing and possibly superconductivity [17].

With a lattice of coupled molecules, one also has to consider the possibility of a cooperative JT effect. This could move the system away from the molecular description. To facilitate hopping between the molecules, it might be advantageous to fix the phase of the distortion from site to site, which conflicts with the dynamic distortion [18]. If band properties dominate the behavior of the system, they could impose a periodic arrangement of distortions, which would possibly open a gap in the electronic structure and turn the system into a band insulator. Thus, it is hard to predict theoretically which limit, band or molecular, might be the most relevant in a given crystalline phase.

Many other questions arise from the introduction of the coupling between the molecules. If JTD are still present in the metal without cooperative order, how will they adapt to a change in the number of electrons on the ball? Will they be fast enough to reach their equilibrium ground state each time this number changes, i.e., on the timescale of the hopping rate? If not, will this tend to fix the number of electrons to the value maximizing the benefit of this particular JTD? In this latter case, the JTD ball would resemble a polaron and could have a significantly higher mass. Some calculations [19] predict that the mass enhancement would be rather small for a polaron but as large as 1,000 for a bipolaron, which means
that these electrons would essentially be trapped by the distortion. This is why it was assumed, early in the discovery of these materials [20], that although JTD offer an obvious source of attraction between electrons, they could not contribute to superconductivity because they would at the same time increase the effective mass by such an amount that electrons would become nearly localized. These authors supposed that JTD would be purely suppressed in the solid. The difficulty here is that there is no obvious limit in which the problem should be treated, and the approximations used in different approaches could all be discussed. The breakdown of the adiabatic approximation in fullerides and the importance of dynamic effects create a particularly intriguing situation.

2 Static Spin-Singlets Stabilized by Jahn–Teller Distortions

2.1 Spin-Singlets in the Cubic Quenched Phase of CsC$_{60}$

The first example we want to present occurs in a cubic phase of CsC$_{60}$, where our NMR study [21, 22] has revealed anomalies, which are very enlightening to address the role of JT-related effects in fullerides. Unfortunately, this phase can only be obtained by quenching, which has limited the number of studies so far.

CsC$_{60}$ has a complicated phase diagram, as illustrated by the behavior of the ESR susceptibility in its different phases shown in Fig. 9. Starting with a high-temperature cubic phase, slow cooling gives rise to a polymeric phase below 300 K, where chains of C$_{60}$ are formed (Fig. 9a). This phase exhibits interesting properties, including an SDW ground state, where low dimensionality could play a role. The JT effect is, however, not expected to play a role there, because the formation of the polymer lifts the degeneracy of the three t$_{1u}$ orbitals and also strongly affects the phonon modes.

To avoid the formation of the polymer, the high-temperature cubic phase can be quenched to low temperatures. Depending on the quenching conditions, two different phases can be observed, one where C$_{60}$ dimers are formed and which is semiconducting (Fig. 9c), the other one with cubic symmetry (Fig. 9b). More precisely, it is simple cubic [23], which means it is orientationally ordered, like C$_{60}$ or Na$_2$CsC$_{60}$ at low temperatures. This latter phase is the subject of this part and will be called cubic quenched (CQ) in the following. It transforms irreversibly into the dimer phase above 130 K. As can be seen in Fig. 9b, its susceptibility is nearly constant (except for a Curie tail at low temperatures), indicating a metallic phase with a relatively high density of states (the value of $\chi$ is comparable to that of K$_3$C$_{60}$). A similar behavior of the ESR susceptibility has been reported [24]. No direct transport measurements are available at present to our knowledge.

Our NMR investigation shows that it is, however, not a simple metal [21, 22]. The biggest anomaly occurs in the $^{133}$Cs NMR spectra shown in Fig. 10 for different temperatures. Two different lines are clearly resolved for all temperatures, with similar intensities, which means they correspond to about the same number of Cs sites. A third much weaker line (6% of the total intensity) can be detected, most clearly at high temperatures (e.g., 120 K) when the lines are well separated.
Fig. 9  ESR susceptibility for CsC\textsubscript{60} exposed to various heat treatments. The metallic quenched phase in b is the one studied in this section. (From [56])
By referring to their position with respect to Cs\(^+\) in a chemical reference (CsCl), i.e., their shift, we will call these lines NS (not shifted), S (shifted), and 2S (twice shifted), respectively. Finding three Cs lines contradicts the expectations of structural studies, for which there is only one site for Cs in this phase, namely the octahedral site \([23]\). We confirmed this by investigating the same sample batch as for the NMR and, in very similar quenching conditions, through x-ray studies at Brookhaven with P.W. Stephens and G.M. Bendele. The particular phase diagram of CsC\(_{60}\) allows one to be convinced rather directly that all these lines are intrinsic: they all disappear irreversibly at the transition to the dimerized structure. In addition, SEDOR experiments \([21]\) demonstrate that the different Cs sites are mixed on the microscopic scale.

We have shown in detail \([22]\) that this spectrum can be very accurately understood by the model presented in Fig. 11, in which some C\(_{60}\) balls are doubly charged, the two electrons being stabilized in a singlet state. The different lines NS, S, and 2S arise from Cs nuclei coupled with 0, 1, or 2 such C\(_{60}\) balls, respectively. From the relative intensities of the lines, we can deduce the number of trapped singlets to be about 10% and also that the singlets are diluted in the structure, as if neighboring C\(_{60}\) were energetically unstable. The position of an

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**Fig. 10** \(^{133}\text{Cs}\) spectra in the cubic quenched phase of CsC\(_{60}\) as a function of temperature
NMR line is proportional to the local electronic susceptibility, and in such a situation, it will be very different for the different sites. For a Cs neighboring a \( \text{C}_6\text{O}^{2-} \), the local electronic susceptibility is dominated by the excitations of the singlet, leading to a strong temperature dependence for the S line clearly seen in Fig. 10. On the contrary, the NS line does not shift, according to the temperature-independent susceptibility characteristic of a metal. A similar contrast is found in the spin–lattice relaxation rate \( 1/T_1 \) for each line. The relatively small number of singlets explains that macroscopic probes, such as ESR, only detect the predominantly metallic character.

The presence of \( \text{C}_6\text{O}^{2-} \) is very surprising considering that the strength of the Coulomb repulsion should, a priori, forbid the double occupancy of a \( \text{C}_6\text{O} \) site. As explained in the introduction, the JT interaction has the opposite tendency and tends to favor evenly charged \( \text{C}_6\text{O} \). The stabilization of the spin-singlet through a JTD is then the most likely explanation. As such, this is an important result, as it proves that JT interactions are important enough to oppose Coulomb repulsion in some cases.

The next question that immediately comes to mind is whether these electrons are trapped on a particular \( \text{C}_6\text{O} \) or may hop from ball to ball. In order to observe two different lines on the NMR spectrum, the singlets must be static during the time needed to acquire the spectrum, in this case a few tens of ms. This is a rather slow timescale implying that they are nearly localized. We can actually estimate the lifetime of a \( \text{C}_6\text{O}^{2-} \) more precisely by making use of a different NMR timescale \( (T_1) \) characterizing the way the spin system comes back to equilibrium after an initial perturbation. In this system, this takes between 30 ms and a few seconds, depending on the temperature. At low temperatures, NS and S have very different relaxation times (reflecting their different electronic environment) but \( 1/T_1 \) changes dramatically above 100 K, and at 130 K the two lines have almost the same \( T_1 \). We attribute this to a motion of the singlet above 100 K, which transforms some S sites in NS sites and vice versa, at a rate still too slow to be observed on the static spectra but fast enough to affect the relaxation processes. Analyzing the \( T_1 \) data along such lines, we may extract the rate of exchange between the two sites, i.e., the lifetime of a \( \text{C}_6\text{O}^{2-} \) as shown in Fig. 12. This lifetime decreases
exponentially with temperature, which sets a new energy scale for the system, characterizing the energy barrier that traps the singlet. It has a magnitude of 320 meV, similar to the activation energies of molecular motions. As the temperature range where the singlets start to move coincides with the onset of molecular motions, this suggests that the singlets may be trapped by some defects of the CQ phase like a misoriented C\textsubscript{60}. By extrapolating this result to higher temperatures, we could expect a \textit{motional narrowing} of the spectrum when it corresponds to the inverse of the frequency separation between the two lines. As indicated by the line in Fig. 12, this would happen at about 150 K, but unfortunately the CQ phase is no longer stable and we cannot check this. Note that in this fast motion limit, the presence of C\textsubscript{60}\textsuperscript{2–} would no longer be detectable on the static spectra, although they could still play a major role in the electronic properties. On the one hand, the gain of energy associated with creating a C\textsubscript{60}\textsuperscript{2–} will help to delocalize electrons, despite the strong Coulomb repulsion. On the other hand, if the electrons participating in a C\textsubscript{60}\textsuperscript{2–} are not to be considered as regular charge carriers, it would mean that the CQ phase is effectively off-stoichiometric, which could have far-reaching consequences for a metal near the Mott–Hubbard transition. Only integer stoichiometries would be Mott–Hubbard insulators in the presence of strong electronic correlations, so that off-stoichiometry would be a way to reconcile the observation of metallicity and the presence of strong electronic correlations. For A\textsubscript{3}C\textsubscript{60}, it has been seriously considered that all compounds could be systematically nonstoichiometric, so that the metallicity and superconductivity would result solely from the nonstoichiometry, which requires a description of these compounds in terms of doped Mott insulators [25]. The properties of CQ-CsC\textsubscript{60} could be discussed in the same spirit.

\textbf{Fig. 12} Lifetime of a C\textsubscript{60}\textsuperscript{2–} in cubic quenched CsC\textsubscript{60} as deduced from the behavior of 1/T\textsubscript{1} for the two lines (see text and [22])
2.2 T, T’ Splitting in A3C<sub>60</sub>

As we will explain here, the idea of nonstoichiometry in A<sub>3</sub>C<sub>60</sub> was mainly based on a puzzling NMR observation: the splitting of the line corresponding to the tetrahedral site in the alkali spectrum, known as “T, T’ splitting” [26–30]. At present, it is not clear whether the T’ line in A<sub>3</sub>C<sub>60</sub> compounds and the S line in the quenched CsC<sub>60</sub> have a similar physical origin, but it is suggestive enough to motivate a reinvestigation of the T’ problem in this light.

In A<sub>3</sub>C<sub>60</sub>, alkali ions fill all interstitial sites of the fcc structure, namely two tetrahedral (T) sites and one octahedral (O) site, so that two lines are expected for alkali NMR with intensities 1:2. However, an additional line, called T’, is observed in the low-T disordered state when the balls do not rotate anymore, with an intensity of about 2:11 in all fcc A<sub>3</sub>C<sub>60</sub> compounds, some examples being given in Fig. 13a. This was first observed by Walstedt et al. [26], who have ruled out through SEDOR experiments that T’ could correspond to phase segregation. These SEDOR techniques are based on detecting dipolar coupling between the nuclei pertaining to the various lines, so the very observation of this effect proves that the sites are mixed on the microscopic scale. These experiments further showed that the T’ site arises from a distorted T site. This means that all the tetrahedral sites are not equivalent, implying that our understanding of the structure of these compounds is simply not correct. More importantly, such a basic problem has led to extensive investigations both by NMR and x-ray but they have not yet been able to pin down clearly the origin of the T’ line.

Many origins have been proposed for the T’ line, ranging from subtle structural distortions to electronic distortions like a charge density wave. Among the structural distortions, Walstedt et al. originally proposed that T’ could be surrounded by misoriented C<sub>60</sub> or be a neighbor of an octahedral site where the alkali atom would be displaced (the Debye–Waller factor for O sites presents some anomalies). SEDOR double-resonance experiments put some very strict con-

![Fig. 13](image-url)  
**Fig. 13** a Example of the T, T’ splitting in K<sub>3</sub>C<sub>60</sub> (39K NMR), Rb<sub>3</sub>C<sub>60</sub> (87Rb and 85Rb NMR), and Rb<sub>2</sub>CsC<sub>60</sub> (133Cs NMR). b SEDOR fraction for 87Rb T sites (open square) and T’ sites (solid square) when another nucleus β is flipped, either 13C (left), 133Cs (right), or 85Rb T’ (inset). The similarity in SEDOR fractions between T and T’ implies that the environment of T and T’ in terms of number and distances of β atoms are nearly identical. (From [30])
straints on what could be the origin of T$`$. Without entering into details, the idea of such experiments is that if the presence of T$`$ results in a different environment of one nuclear species $\alpha$ in terms of another spin species $\beta$, it should be detectable. The environment of the $\alpha$ species is characterized by a “SEDOR fraction”, proportional to $\Sigma_{\beta} 1/r^6$, where $r$ is the distance between $\alpha$ and $\beta$. The accuracy of such experiments comes from the strong dependence of the dipolar coupling on distance. As shown in Fig. 13b, the main result is that the SEDOR fractions are very similar for all couples of nuclei and this excludes many possibilities for the origin of T$`$. If T$`$ were a neighbor of a misoriented C$_{60}$, so that it would see a pentagon instead of an hexagon, the difference in the number of $^{13}$C first neighbors should be observed in the $^{13}$C SEDOR fraction. If T$`$ were a neighbor of an off-centered alkali in a neighboring O site, this slightly smaller distance should be observed in the $^{133}$Cs SEDOR fraction. If, for some reason, T$`$ had more T$`$ neighbors than T, it should be observed as a different T$`$ SEDOR fraction. The fact that it is not (inset of Fig. 13b) excludes a “clustering” of the T$`$ sites and more general situations where T$`$ is a neighbor of some defect, which leads naturally to clustering.

Rather than these structural distortions, x-ray data have led to the proposal [31] that T$`$ could be a neighbor of an alkali vacancy. Indeed, Rietveld refinements seem to require a systematic off-stoichiometry of A$_3$C$_{60}$, being in fact A$_{3-e}$C$_{60}$ with $\varepsilon=0.07\pm0.03$ (occurring preferentially in a tetrahedral site). The relative intensities of the T and T$`$ lines fit well into this picture for $\varepsilon=0.06$. However, this interpretation does not fit with more recent NMR experiments. In A$_3$C$_{60}$, like in CQ-CsC$_{60}$, the tetrahedral site alkali NMR spectra are motionally narrowed into a single line with increasing temperature. This indicates that the T$`$ sites, as the S sites in CQ-CsC$_{60}$, “move” at high temperature. The timescale of this motion has been studied in detail by Zimmer et al. through two-dimensional NMR exchange experiments [28]. Pennington et al. argued [30] that, if T$`$ is related to vacancies, the “motion” of T$`$ should be associated with a diffusion of Rb atoms through the vacancies, which should be detectable through appropriate double-resonance experiments. In Rb$_2$CsC$_{60}$, they used the NMR of the $^{133}$Cs atom in O sites as a probe of this Rb motion. Indeed, the Cs atom is sensitive to the presence of a Rb atom in neighboring T sites, through the dipolar coupling between their nuclear spins. If one Rb atom moves on the timescale of the measurement, the dipolar coupling is lost and, under certain observation conditions, this reduces the intensity of the Cs NMR signal. Such a loss of intensity was not detected at temperatures where the Rb diffusion should take place according to the vacancy model. This quite directly refutes such an interpretation.

All the atomic and structural defects examined so far to explain this T$`$ line have apparently been excluded by this set of experiments. The case of CQ-CsC$_{60}$ suggests an alternative origin, that T$`$ is a neighbor of an electronic defect, such as a small fraction (about 3%) of localized C$_{60}^2$- or C$_{60}^4$-. In CQ-CsC$_{60}$, the assignment of a charged C$_{60}^2$ was made possible because its different electronic properties could be distinguished through marked differences in both T dependences of the shift and spin–lattice relaxation time $T_1$ for the NS, S, and 2S lines. This is not as easy in A$_3$C$_{60}$, as the differences between T and T$`$ lines are experimentally much weaker. Although the splitting of the spectra is most easily detected on
tetrahedral sites in \( A_3C_{60} \), a splitting of the octahedral line has been detected in \( Rb_3C_{60} \) by magic angle spinning \( [28] \), suggesting that both sites are sensitive to the local modification. The fact that the coupling with a \( C_2^{2n} \) would be smaller for O sites than T sites is understandable because the distances are larger and there are more neighbors, which averages the effect. Compared to QC-CsC\(_{60}\), where Cs is in an O site, the splitting is much smaller, implying that the coupling to a localized \( C_2^{2n} \) in \( A_3C_{60} \) would be weaker than in CQ-CsC\(_{60}\).

This interpretation is, however, apparently in conflict with the absence of clustering detected in SEDOR experiments. A \( C_2^{2n} \) would create eight T’ sites, among which four are nearest neighbors. This gives automatically three T’ neighbors to a T’ site, which is higher than the statistical probability of being T’. Whether this “clustering” would be detectable by SEDOR should be checked carefully; the contribution of second neighbors to the SEDOR fraction could go in the opposite direction, especially if \( C_2^{2n} \) tend to dilute in the lattice like they do in QC-CsC\(_{60}\). Let us also note that from the technical point of view, the distinction between SEDOR fractions of T and T’ sites is by far the most difficult to establish, as it requires one to selectively excite T’ or T, which are very close in frequency, contrary to the cases of \(^{13}\text{C}\) or \(^{133}\text{Cs}\), and the efficiency of this selective excitation should be calibrated before concluding. We note that the formation of static \( C_2^{2n} \) would be an alternative way to reach off-stoichiometry without an actual chemical nonstoichiometry of the material.

3 Mott–Jahn–Teller Insulators

From the discussion of the JT effect presented in the introduction, one can expect a simplest situation when there is no conflict between JT and Coulomb repulsion regarding the optimal number of electrons per ball, i.e., for evenly charged \( C_{60} \). In this case, both interactions tend to localize an equal number of electrons on each ball, albeit with a different spin state. We will show that, as for the free \( C_{60} \), a low spin state is favored in Na\(_4\)C\(_{60}\) and A\(_4\)C\(_{60}\) (A=K, Rb), making it very likely that JT effects are present. The JTD itself has, however, remained elusive. On the other hand, these compounds are insulating which cannot be accounted for by the presence of JTD alone. The origin of this insulating state will be discussed in connection with a metal–insulator transition observed by applying pressure to Rb\(_4\)C\(_{60}\). This adds insight into the relation between metallicity and JTD, which is a crucial issue.

3.1 Gaps Detected in Na\(_2\)C\(_{60}\) and A\(_4\)C\(_{60}\)

Among \( A_nC_{60} \), \( n=4 \) is in general stable but compared to the cubic \( A_3C_{60} \), the structure has to distort to body-centered tetragonal to accommodate the large alkali ions (A=K, Rb, Cs). Band calculations have very early on shown that there is little change of the band structure associated with this distortion \( [32] \), but other influences of this particular structure on the electronic properties can be questioned. With the small Na atom, the structure for Na\(_4\)C\(_{60}\) remains fcc at high tem-
perature but this phase polymerizes below 300 K, which leaves a relatively small
temperature range to study the properties of the cubic phase [33]. On the other
hand, \( n=2 \) is not obtained with large alkali ions (K, Rb, Cs) but is stable for \( \text{Na}_2\text{C}_{60} \)
at all temperatures (with the two Na atoms in tetrahedral sites). As \( n=2 \) and 4 are
symmetric with respect to half-filling in the \( t_{1u} \) band, similar properties would be
expected unless extrinsic parameters, like details of the structure, play a major
role. A comparative study of \( \text{Na}_2\text{C}_{60} \) and \( \text{A}_4\text{C}_{60} \) is then desirable.

Figure 14 presents the temperature dependence of the spin–lattice relaxation
rate \( 1/T_1 \) in \( \text{Na}_2\text{C}_{60} \) and \( \text{K}_4\text{C}_{60} \) for \( ^{13}\text{C} \) NMR [34]. The very similar behavior
observed in the two compounds establishes readily that the electron–hole sym-
metries hold, despite the change in structure. Below room temperature, \( 1/T_1 \) is
dominated by an activated behavior, sketched by the solid line. The main source
of relaxation for NMR nuclei is due to their coupling with unpaired electrons
when present. At first sight, this activated behavior means that there are no
unpaired electrons at low temperatures but that such states can be thermally
populated, i.e., there is a gap in the electronic structure. The gap measured here
is of 60 meV in \( \text{K}_4\text{C}_{60} \) and 140 meV in \( \text{Na}_2\text{C}_{60} \), in agreement with other magnetic
measurements [35–37]. Above room temperature, the behavior obviously devi-
ates from the activated law, which will be discussed later.

The singlet ground state is confirmed by the NMR spectra that are not broad-
ened at low temperatures by static local magnetic fields. It can be understood by
introducing JTD of the \( \text{C}_{60} \) molecules that favor this nonmagnetic ground state,
as we have already seen for the \( \text{C}_{60}^{2-} \) ion. A rapid look at the situation gives the
impression that, once JTD are introduced, they will lift the degeneracy between
the \( t_{1u} \) levels, and compounds with an even number of electrons would be turned
into trivial band insulators, explaining that \( \text{A}_4\text{C}_{60} \) is an insulator contrary to \( \text{A}_3\text{C}_{60} \).
This reasoning is, however, wrong because the gap opened by JTD is rather small

![13 C NMR](image)

**Fig. 14**  \( 1/T_1 \) as a function of temperature for \( \text{Na}_2\text{C}_{60} \) and \( \text{K}_4\text{C}_{60} \). The peak at 175 K in \( \text{Na}_2\text{C}_{60} \) is
due to a contribution from molecular motions and is irrelevant for the electronic properties
(calculated to be at most 500 meV) and should easily be closed by the formation of a band of typically 500 meV width. As a matter of fact, the gaps measured here are even much smaller. We are then in a tricky situation where we would not expect JTD to be stable in the solid (on their energy scale, the electronic levels cannot be considered as degenerate, except at the center of the Brillouin zone), but we need them to explain the nonmagnetic ground state. In addition, even if present, they should not turn these systems into insulators, although this is the most prominent feature to explain.

The insulating character of A₄C₆₀ is better addressed by studying transport properties directly [38, 39], as for example their optical conductivity presented in Fig. 15. The difference between K₃C₆₀ and K₄C₆₀ is clearly seen; the conductivity of K₃C₆₀ increases at low energy, as expected for a metal, while the one of K₄C₆₀ decreases, as the Drude peak is lost. A peak at 1 eV is present in both compounds and corresponds to interband excitation from t₁u to t₁g, in agreement with band structure calculations. The first peak in K₄C₆₀ occurs at 0.5 eV, a very large gap compared to the one detected by NMR, but more consistent with the gap predicted theoretically for the JT splitting.

Fabrizio et al. [18] recognized that transport measurements, such as optical conductivity or EELS [40], all measure a large “optical gap”, while magnetic probes, like NMR or SQUID [37] and ESR [35] measure a much smaller “spin gap”. The optical gap was attributed to the direct gap opened by the JTD between the t₁u levels, while the spin gap corresponds to singlet–triplet transition between two different JTD as discussed previously. The remarkable fact is that the order of magnitude of these two gaps corresponds very well to the JT framework, which can hardly be a coincidence and strongly supports this model, as opposed to models based on charge density wave or purely Coulombic localization. Within this model, the gap could be very small or nonexistent in certain directions,

![Fig. 15](image-url)  
Fig. 15 Optical conductivity of K₃C₆₀ and K₄C₆₀ illustrating the disappearance of the Drude term in K₄C₆₀. The peak at 1 eV is due to interband transitions. The strong peak at 0.5 eV in K₄C₆₀ corresponds to the gap seen by transport. (From [38])
and these systems would remain metallic if strong electronic correlations were not present. This is why Fabrizio et al. proposed to call these systems “Mott–JT insulators”.

Direct evidence for a JTD in this phase has, however, been hard to establish. A thorough x-ray investigation has been performed for Rb$_4$C$_{60}$, which sets a maximum of 0.04 Å for the anisotropy between the diameters of the molecule in different directions [41]. This error bar is of the order of magnitude of the distortion observed in fulleride salts, so it is not very conclusive in itself. The fact that no superstructure is observed in this study further means that JTD, if present, do not adopt a long-range order. Consequently, the insulating state is unlikely to result from a band property, like a gap opened by a commensurate cooperative distortion. The JTD is more likely dynamic, like in the Mott–JT scenario.

Another approach to detect the distortion is to search for modifications of the vibrational spectrum. A splitting of the T$_{1u}(4)$ infrared active mode has been detected at room temperature in K$_4$C$_{60}$ and Rb$_4$C$_{60}$ [38]. This could be the signature of a static JTD but also a consequence of the lower symmetry of the bct structure. To our knowledge, there is no similar study for Na$_2$C$_{60}$. Very recently, Kamaras et al. investigated the temperature dependence of this mode [42] and Fig. 16 shows a clear evolution between 200 and 300 K from a doublet to a triplet splitting. The threefold splitting of T$_{1u}$ is a clear signature of biaxial symmetry. Here again, it could be due to a modification of the structure or of the JTD (or both, as the two are certainly related). No structural transition has been reported in this temperature range but Kamaras et al. mention that it would be consistent

![Fig. 16](image)

**Fig. 16** Modification of the T$_{1u}(4)$ infrared active mode with temperature in K$_4$C$_{60}$. (From [42])
with an orientational transition that cannot be excluded at present. The splitting could also be explained by a D$_{2h}$ JTD, which happens to be the one that would be stabilized by the crystal field of the bct structure. In this case, the change at 300 K suggests that the JTD evolves from a dynamic to static status (on the fast timescale of the IR experiment of about $10^{-13}$ s). Alternatively, it could be due to disorder between different JTD at 300 K. Interestingly, a saturation of $1/T_1$ is observed around 250 K (Fig. 14) that suggests this change is also affecting the electronic properties.

3.2 Connection Between Metallic and Insulating Phases

An alternative way to clarify the nature of this state is to test its stability with respect to a metal–insulator transition. This has received a lot of theoretical attention recently. The JT singlet ground state makes these compounds free from the tendency towards a magnetic instability observed in so many Mott insulators. In fact, their ground state does not break any symmetry and Capone et al. explained [43] that it then has a zero entropy, which makes a direct connection with a metal impossible (it would violate the Luttinger theorem). These authors predict that the only way to go from the insulator to the metal would be through an exotic superconducting phase or a first-order transition.

Experimentally, a metal–insulator transition has been observed between 8 and 12 kbar in Rb$_4$C$_{60}$ through NMR [44]. This is illustrated in Fig. 17 by the temperature dependence of $1/T_1$ for different pressures. While the behavior at 1 bar is dominated by an activated component, very similar to the one of K$_4$C$_{60}$ in Fig. 14, it gradually evolves towards a linear behavior, which is characteristic of a metal. This is the so-called Korringa law where the slope is proportional to $n(E_f)^2$.

Remarkably, the pressure needed to close the gap is quite modest, consistent with the idea that the indirect gap in the band structure could indeed be quite small. To date, this is the only report about such a transition.

Looking more closely at the evolution of $1/T_1$ at low temperatures, it is interesting to note that there seems to be a coexistence between the insulating and metallic behavior at 8 kbar. For low temperatures, the behavior is linear like in a metallic state with a relatively low density of states (this would correspond to $\chi=3.10^{-4}$ emu/mol) but it increases more steeply up to room temperature, as if the singlet–triplet transitions were still present in the metal.

This coexistence appears in contradiction to the sharp transition expected theoretically, and could be a clue to understanding the survival of JTD in the metal as witnessed in CQ-CsC$_{60}$. By examining carefully the low-temperature behavior of $1/T_1/T$, where the metallic term, if present, should dominate, we did not detect any deviation from the activated behavior down to the lowest measured temperature in K$_4$C$_{60}$. On the other hand, in Na$_2$C$_{60}$ there is a clear deviation and $1/T_1/T$ is nearly constant below 100 K; also its value is small, as can be seen in the inset of Fig. 18. Because of the small size of the Na atom, the distance between C$_{60}$ in this phase is smaller than in K$_4$C$_{60}$ and probably similar to Rb$_4$C$_{60}$ at some moderate applied pressure. This suggests a correlation between the size of the metallic component and the distance between C$_{60}$ balls, which supports
a Mott–Hubbard transition. Let us recall that Na₄C₆₀, the compound with the smallest distance between balls, was said to be metallic [33] because of a Pauli-like susceptibility at high temperature, which also fits in this picture. Finally, there also seems to be a correlation between the strength of the metallic component (determined by the value of $1/T_1$ at low temperature) and the nearly constant value of $1/T_1$ reached at high $T$, as sketched in Fig. 18 (the comparatively smaller value of Na₂C₆₀ is due to the larger gap for this compound). The reduced value of $1/T_1$ at 300 K in the most metallic compounds could be explained by a smaller number of triplet states and/or a shorter lifetime of these excited states. The coexistence between the two phenomena is however quite robust, since Rb₄C₆₀ at 12 kbar is a good metal, with a density of states comparable to the one of Rb₃C₆₀.

Fig. 17 ¹³C NMR $1/T_1$ in Rb₄C₆₀ as a function of applied pressure. The activated behavior at 1 bar is characteristic of the insulator while the linear temperature dependence at 12 kbar is characteristic of a metal. (From [44])
4 Dynamic Spin-Singlets Stabilized by Jahn–Teller Distortions

4.1 Metal–Insulator Transition Between $n=3$ and $n=2$ or 4

The insulating nature of $A_4C_{60}$ is best understood as resulting primarily from rather large electronic correlations. With the known values for $U$ and $W$ in these systems, this is in fact what could be expected. The puzzling fact remains the opposite behavior of $A_3C_{60}$. The metallic nature of $A_3C_{60}$ alone could be reconciled with a rather strong value for $U$, by taking into account the degeneracy of the band, which shifts the critical ratio for the metal–insulator transition to a higher value by a factor $\frac{1}{\sqrt{N}}$, $N$ being the degeneracy [45]. This can be understood intuitively by the fact that there are more possibilities in a degenerate band for one electron to hop to the next site which facilitates this process. But $U/W$ is very similar for both compounds, so that degeneracy does not explain their opposite behaviors consistently. The problem of metal–insulator transition in degenerate systems as a function of band filling has actually received a lot of theoretical attention recently [46–48]. Most interesting systems exhibit orbital degeneracies, so that it is a very general problem and fullerides could help to modelize this, thanks to their rather simple band structure. Quantum Monte Carlo simulations predict a dependence of the critical ratio on doping (see Fig. 19) and an asymmetry with respect to half filling. The half-filled band is not the most strongly correlated, as it can withstand higher values of $U$ before a transition occurs. This is because the enhancement introduced by degeneracy is optimal in a symmetric situation between hole and electron hopping, i.e., for half filling. However,
$A_3C_{60}$ and $A_4C_{60}$ would have very similar critical $U/W$ ratios, so this calculation does not really solve the problem. We quote it mainly to illustrate how the opposition between $A_3C_{60}$ and $A_4C_{60}$ raises fundamental questions. Also, it predicts that $A_1C_{60}$ should become insulating the most easily, although we have seen that the cubic quenched CsC$_{60}$ behaves as a rather good metal. The opposition between odd and even stoichiometries seems to be more decisive for the metallic nature than the position with respect to half filling.

The JTD present precisely the advantage to make a clear distinction between even and odd stoichiometries. Up to now, we have seen them acting in CsC$_{60}$ as a sort of defect localizing electrons. Within this picture, their main consequence at the macroscopic level could be the related nonstoichiometry of the metal. Many properties of alkali fullerides (particularly of the most studied $A_3C_{60}$) are well described by band-structure calculations, for example the density of states deduced from the Pauli susceptibility, and it seems somewhat unlikely that such a huge misunderstanding of the actual number of carriers in these materials could have remained unnoticed for such a long time. One of the strongest objections to the nonstoichiometry of $A_3C_{60}$ is that $T_c$ is peaked at three electrons per $C_{60}$, as shown by Yldirim et al. [49]. We note that the interpretation of such an experiment would not be straightforward with a JTD-induced nonstoichiometry, as it is not a simple matter to predict the number of carriers that would be introduced by JTD as a function of $n$.

On the other hand, we have observed while studying even stoichiometries that JTD do not imply strict localization but, on the contrary, seem to survive rather easily in the metallic state. Trapping in CsC$_{60}$ is then more probably due to defects than to a large polaron-like effective mass that would be intrinsic to a JT-distorted $C_{60}^2$. One can then wonder about other types of influence of JTD in metallic compounds.
4.2 Dynamic Spin-Singlets in A$_3$C$_{60}$

Despite the expected strongly correlated nature of A$_3$C$_{60}$, there have not been so many reports of anomalous behaviors, which led many people to assume finally that these systems are relatively conventional metals. We present here very clear anomalies in the NMR behavior of these compounds. Figure 20 shows $1/T_1$ for $^{13}$C NMR in two superconducting compounds, Rb$_3$C$_{60}$ ($T_c=28$ K) and Na$_2$CsC$_{60}$ ($T_c=12$ K). Both compounds are cubic but Rb$_3$C$_{60}$ is orientationally disordered at all temperatures, while there is an orientational transition in Na$_2$CsC$_{60}$ at 300 K. We observe strong deviations from the linear $T$ dependence expected for a simple metal. This tendency has actually been observed in many A$_3$C$_{60}$ systems and seems to be the rule [50–52]. The deviation is step-like, and its amplitude is modest in Rb$_3$C$_{60}$, where $1/T_1$ increases by 30% between 100 and 300 K, but very sizable in Na$_2$CsC$_{60}$, where $1/T_1$ is multiplied by three in the same temperature range (note that the orientational transition at 300 K cannot play a role in this since most of the increase occurs below room temperature). The first impulse would be to explain these deviations by refining the Korringa law, for example by including a change of the density of states with temperature due to the lattice expansion, which can be quite sensible in fullerides. However, we have found that such explanations cannot account for the huge deviation in Na$_2$CsC$_{60}$, which can only be understood if another very efficient relaxation mechanism is present.

There are, of course, a wide range of relaxation processes that could a priori contribute to the relaxation. A striking fact is that the deviation seen in Na$_2$CsC$_{60}$ mimics the relaxation behavior of Na$_2$C$_{60}$, as evidenced in Fig. 21 [34]. In the case of Na$_2$C$_{60}$, there is little doubt that the relaxation is due to the electronic triplet state formed on a JT-distorted C$_{60}^2$–, otherwise all the comparisons with A$_4$C$_{60}$ would become meaningless. It is natural to attribute the deviation in Na$_2$CsC$_{60}$ to

![Image of figure 20](image-url)

**Fig. 20** $^{13}$C NMR $1/T_1$ as a function of temperature for Rb$_3$C$_{60}$ and Na$_2$CsC$_{60}$. For a typical metal, $1/T_1$=cst is expected and the strong deviation observed here is attributed to singlet–triplet transitions of JT-distorted C$_{60}^2$– and C$_{60}^4$–.
similar molecular excitations. This relaxation process is very efficient because the NMR nuclei couple strongly to the fluctuations of a localized electronic spin. Actually, it does not need to be strictly localized, it is sufficient that it is formed for a sufficiently long time to render significant the probability that an NMR nucleus witnesses an electronic flip. In a simple metal, the hopping rate is such that an electronic spin could never be considered as localized; its individual magnetism disappears to the profit of the Pauli susceptibility of the Fermi sea. In fullerides, the situation is not so simple as the strong correlations tend to increase the time spent by one electron in the vicinity of a \( C_{60} \) ball. The case of \( Na_2C_{60} \) or \( Rb_4C_{60} \) under pressure does indeed suggest that molecular excitations may coexist with some metallic character.

There are various substructures within the \( t_{1u} \) levels of a \( C_{60}^3^- \) due to electronic correlations and/or the JT effect that could promote the formation of one preferential spin value. To explain our data, we need two molecular configurations separated by a gap of the order of 140 meV, the lowest one being nonmagnetic (as there is no deviation at low \( T \)) and the highest one magnetic. With three electrons on a ball, the only possible transition would be between \( S=1/2 \) and \( S=3/2 \). This is problematic, as both should give rise to substantial relaxation (it would only be slightly less efficient for \( S=1/2 \), proportionally to the difference in susceptibility). To obtain a nonmagnetic ground state, one has to pair electrons in a \( C_{60}^2^- \) or \( C_{60}^4^- \). In a metal with an average number of three electrons per ball, there is always a nonnegligible probability to find such units. They would not be expected to dominate the NMR behavior, unless their lifetime is particularly long, and in this case the stabilization of JTD offers a very plausible way to explain such a phenomenon. Following this idea, the similarity between \( Na_2C_{60} \) and \( Na_2CsC_{60} \) is directly explained. We conclude that the deviation from the Korringa law in \( A_3C_{60} \) arises from the enhanced stability of dynamic JT-distorted \( C_{60}^2^- \) and \( C_{60}^4^- \).

To test this assumption, one can extract the characteristic fluctuation time \( \tau \) for the electronic spins from the \( 1/T_1 \) data, by assuming \( 1/T_1 \propto \chi \tau \), where \( \chi \) is the

---

**Fig. 21** Comparison of \( ^{13}C \) NMR \( 1/T_1 \) for \( Na_2C_{60} \) and \( Na_2CsC_{60} \). The very similar behavior observed despite the different electronic properties is a key to identifying the origin of the nonmetallic behavior of \( Na_2CsC_{60} \).
susceptibility of the “localized spin” [53]. We find typical timescales of the order of $t = 10^{-14}$ s, which is comparable to the hopping rate in these systems and is then consistent with the metallic character. We argue [54] that the electronic spin would be likely to be relaxed by conduction electrons, which makes it easier to detect in systems with low density of states like in Na$_2$CsC$_{60}$. A simple model relating $t$ to $n(E_f)$ supports this hypothesis as it describes very well the difference between Rb$_3$C$_{60}$ and Na$_2$CsC$_{60}$ as well as, more generally, the evolution of the insulating compound into a metallic one, as in Rb$_4$C$_{60}$ as a function of applied pressure. This is an extension of the trend already apparent in Fig. 18.

It would be nice to obtain a more direct proof of the presence of JTD and/or charge segregation in these systems. Unfortunately, all the results presented in this review so far show how difficult it is to detect these distortions directly, even in apparently much more favorable cases, so that it is bound to be extremely difficult. Local probes with very fast timescales would be required. In this context, it is interesting to note that in the optical data of Fig. 15, a better fit is obtained by using a Lorentz component centered at 0.5 eV like for A$_4$C$_{60}$, where it represents the direct gap of the JTD. These authors suggested it could be a sign for the presence of JTD in A$_3$C$_{60}$ as well.

4.3 High-Temperature Properties of Fullerides

Finally, we would like to mention some anomalies observed in certain phases at high temperature, mainly CsC$_{60}$ and Na$_2$CsC$_{60}$. They are not completely understood but they strongly suggest that these compounds become insulating above room temperature. Such a behavior must contain by default some clues about the cooperation needed between the different parameters to obtain a metallic state.

When studying the cubic quenched phase of CsC$_{60}$, we reached a point just before the transition to the dimer at 130 K where the spin-singlets started to move. Note that the number of NS sites, equivalently of C$_{60}^{2-}$, was not changing dramatically at the same time, suggesting that the C$_{60}^{2-}$ move but do not disappear. This suggests that, if stable, this phase would become quite comparable to A$_3$C$_{60}$: a metallic phase with a tendency to form electronic pairs induced by JTD. As it is the only metallic phase besides A$_3$C$_{60}$ for cubic fullerides, this comparison is crucial. However, when the cubic phase is stable again, above 400 K, Fig. 9 shows that the ESR susceptibility is strongly temperature dependent. This resembles a Curie behavior much more than a metallic one and suggests that electrons are localized. What happened?

In Na$_2$CsC$_{60}$ a similar metal–insulator transition was suggested [55]. The ESR susceptibility is Curie-like and the value of the reflectivity at low frequencies, shown in Fig. 22, decreases sharply between 200 and 300 K. Whereas it behaves like a metal at low temperature, approaching total reflection in the limit of low frequencies, it is not the case anymore at 300 K. A change in the relaxation behavior is also clear from Fig. 20 and other NMR signs of a progressive localization of charge carriers have been detected [54]. All of this suggests a metal–insulator transition took place slightly below room temperature.
Together, these two observations suggest that it would not be uncommon for a metallic fulleride to become insulating at high temperatures. This reminds us of other high-temperature anomalies reported in the literature. In Rb$_3$C$_{60}$, the photoemission spectra do not display a sharp Fermi edge above 400 K (in this compound, a slight decrease of $1/T_1 T$ above 500 K can be noted in Fig. 20 although it is not dramatic). In addition, the absence of saturation in the resistivity at high temperature, commonly observed in A$_3$C$_{60}$, yields such small values for the mean free path that it seems counterintuitive that these compounds remain metallic.

In this review, we have argued that the metallicity is intimately connected to the presence of JTD. We could speculate that the population of many different JTD states at high temperatures introduces a form of disorder that could trigger a metal–insulator transition of the Anderson type. It reveals conversely that cooperation is required between JTD and the electronic motion to establish coherent band-like properties. The transition at 250 K in K$_4$C$_{60}$ shows that the nature of the distortion can change, a situation close to that of the fulleride salt. A similar transition in metallic compounds might be responsible for the destabilization of the metallic state.

5 Conclusion

To summarize, we have proposed in this paper that the metallic or insulating nature of fullerides depends primarily on the parity of the number of electrons transferred to the C$_{60}$ molecule. We attribute this to the influence of JTD. As they are more favorable for evenly charged C$_{60}$, they tend to induce attractive correlations in odd-electron systems that promote the formation of pairs of electrons and help to overcome the strong Coulomb repulsion. This reasoning is based on the comparative behavior of systems with an odd or even number of electrons per C$_{60}$. 

Fig. 22  Infrared reflectivity of a powder sample of Na$_2$CsC$_{60}$. A Lorentz Drude peak is shown for 20 and 200 K; but at 300 K, the metallic behavior is lost. (From [55])
Systems with an even number of electrons, such as Na$_2$C$_{60}$ or A$_4$C$_{60}$ (A=K, Rb) are insulating, contrary to the prediction of band calculations. This insulating state is best described by assuming the presence of JTD. Although they have not been directly detected, they explain consistently many features of this state: the nonmagnetic ground state and a different gap seen in transport measurement (500 meV) or magnetic measurement (100 meV).

It is, however, not the JTD that turn these systems into insulators but strong correlations. The nature of metal–insulator transitions in these systems is one of the most debated points at present. Experimentally, a metal–insulator transition can be induced by relatively modest pressure in Rb$_4$C$_{60}$ and in the compound with the smallest lattice parameters (Na$_2$C$_{60}$) a residual metallic character can be detected. These behaviors support the idea that these compounds lie on the border of a Mott–Hubbard transition. We still observe typical molecular excitations of JT-distorted C$_{60}$ on the metallic side of the transition, suggesting a possible coexistence.

This motivates a study of JTD in metallic fullerides. We observe two different cases, where pairs of electrons are formed but they can be either nearly localized (cubic quenched phase of CsC$_{60}$) or very dynamic (on timescales of about $10^{-14}$ s in A$_4$C$_{60}$). This supports the idea that JTD may induce attractive interactions among electrons in odd-electron systems and raises the question of the exact interplay of such an interaction with band properties. In CsC$_{60}$, the spin-singlets seem to be trapped by defects, maybe related to misoriented C$_{60}$ not present in A$_4$C$_{60}$. However, in both cases, anomalies are detected at high temperature suggesting that some of these phases become insulating. Some correlation seems to be required between the molecular excitations to establish a coherent band-like transport, and it might be lost at high temperatures. The understanding of this connection would certainly be of great interest, not only for the fullerides community, but more generally to study all systems with degenerate bands, where the occurrence of JTD is always a possibility that complicates the analysis of strong correlations.

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6 References

NMR Studies of Insulating, Metallic, and Superconducting Fullerides

Charge Transfer and Bonding in Endohedral Fullerenes from High-Energy Spectroscopy

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Abstract This contribution deals with the investigation of charge transfer and bonding in endohedral fullerenes in the solid state using high-energy spectroscopies such as photoemission and x-ray absorption. An overview is given of the detailed and direct information that can be won as regards the valence state of the encapsulated species, the degree of hybridisation between the electronic states of the endohedral entity and the carbon cage and finally the charge transfer between the host and guest. Examples are presented of rare-earth monometallofullerenes, rare-earth and transition-metal dimetallofullerenes and endohedrals containing transition-metal-nitride clusters, both in the pristine state and intercalated with alkali metals.

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1 Introduction

Fullerenes have come to enjoy a special status, not only in the physics and chemistry research communities, but also outside the confines of academic or industrial R&D. The beauty of C₆₀’s truncated icosahedral form and its similarity with the object of attention in the world’s favourite sport make the fullerenes’ best known ambassador the most widely recognised molecular structure. The intrinsic elegance of the fullerenes’ molecular architecture is matched by the breathtakingly broad spectrum of physical properties they exhibit. Through only marginal alteration of their crystal structure and π-electron density, solid C₆₀-based compounds offer the researcher access to insulating, semiconducting, metallic, superconducting, ferro- and antiferromagnetic ground states. Here the outstanding challenge is the development of a self-consistent description of the fundamental physics underlying this electronic gymnastics – all the more exceptional considering that the systems in question possess neither d nor f electrons. A number of such issues form the focus of chapters contained within this volume. In this chapter, we direct the reader’s attention to another special property of the fullerenes: their ability to encage atoms, ions or clusters within the confines of their carbon cage structure to give endohedral fullerenes. In the following, we deal with the results of experiments aimed at investigating the charge transfer and interactions between the encapsulated species and the host carbon cage in solids built up of endohedral fullerenes. The experimental approach we choose is that of using electron spectroscopies, also known as high-energy spectroscopies. Such probes offer three main advantages: (i) they represent a very direct monitor of the electronic states resulting from the overlap of the frontier orbitals, which essentially control the physical properties of the endohedral system in question; (ii) either via exploitation of photoionisation cross sections or the use of excitations involving the site-specificity of core levels, they offer selective access to either the electronic states of the encapsulated species or those of the carbon host; and (iii) in combination with molecular-beam film deposition methods, they are able to deal with quite small quantities of endohedral material (down to 200 µg) – a significant advantage considering the time-consuming nature of the extraction of pure endohedral fullerenes from mixed (metallo)fullerene soot using multicycle HPLC and the consequent scarcity of the highly pure fullerene material required for high-level research.

This chapter is by no means an exhaustive review of research into endohedral fullerenes, but is rather intended to give the reader a glimpse of the novel and exotic electronic world hidden behind the shell of each fullerene cage. After an experimental section, dealing very briefly with endohedral synthesis, the film preparation and relating the salient points of the high-energy spectroscopic measurements, the chapter continues with a series of sections covering results and their interpretation for different varieties of metallofullerenes. A summary of the current status of research into charge transfer and bonding in endohedral fullerenes follows, and finally an outlook is offered, indicating the direction current trends are taking endohedral research.
2 Experimental

2.1 Endohedral Fullene Synthesis and Film Preparation

All the endohedral fullerene samples studied here were produced using a modified carbon-arc method [1]. In this method, an arc is set up between a pair (or a number of) graphite electrodes, which have been hollowed out and filled with either an oxide or other carrier of the metal species that is intended to be encapsulated inside the fullerene cages. The electrodes are housed in a vacuum chamber back-filled with He gas, and the raw soot generated by the arc is collected for purification. Raw endohedral fullerene soot generally contains endohedral fullerenes only as a minority product, and thus the non-fullerene soot and the non-endohedral fullerenes (‘empty’ C_{60}, C_{70}, C_{76}, C_{84} etc.) have to be removed and the endohedral of choice (e.g. M@C_{82} [2], where M stands for a metal such as yttrium) is thereby purified to a level of >95%. All of the metallofullerenes studied here were supplied either by Nori Shinohara’s group in Nagoya University, Japan [3], or by Lothar Dunsch’s group at the IFW in Dresden [4].

In order to obtain clean thin films suitable for high-energy spectroscopic studies, the endohedral fullerene in question was sublimed in ultrahigh vacuum (UHV) from a resistively heated effusion cell, specially designed to cope with the small quantities of material involved. The substrate was generally a clean metal surface, prepared either in the form of a freshly evaporated film, a sputtered gold foil, or a single crystal of Au, Ag or Cu cleaned by cycles of sputtering and annealing. In all cases, the fullerene films were transferred from the preparation chamber without breaking UHV into the spectrometer chamber in which the analysis took place. In some cases, the only moderate thermal stability of the endohedral fullerenes did not allow for extended out-gassing of the evaporator, and the film had to be deposited by a ‘shock’ evaporation method with rapid ramping of the crucible temperature to 600–650 °C for a brief period of time. Fullerene film thicknesses were of the order of several tens to hundreds of nanometres.

2.2 High-Energy Spectroscopies

Figure 1 illustrates in cartoon form the elementary processes upon which the various high-energy spectroscopies used are based. The excitation involved in each case is either initiated by absorption of a photon (vacuum ultraviolet or soft x-ray) or transfer of energy (and momentum) from a high-energy electron beam.

It would be out of place here to burden the reader with a detailed treatment of the physics underlying the spectroscopies sketched in Fig. 1. The physical quantities measured are better dealt with at the point at which the data are presented and discussed. The experiments themselves were carried out using a variety of apparatus, located at various laboratories.
2.2.1 Laboratory-Based Photoemission

Valence and core-level photoemission experiments were carried out in the IFW Dresden under the following conditions. Unless otherwise stated, the valence band photoemission data were recorded at room temperature using He:Ια radiation (21.22 eV) with a total energy resolution of 100 meV, and the core-level photoemission data, using monochromatised Al:Κα radiation (1486.6 eV) with a total energy resolution of 0.4 eV. All such data are angle-integrated in nature (±4° or more).

2.2.2 Synchrotron-Based Measurements

The resonant photoemission and x-ray absorption experiments took place at the synchrotron radiation facilities ELETTRA (Trieste, Italy) or BESSY (Berlin, Germany). At ELETTRA, the VUV-photoemission and SuperESCA beamlines were used, and at BESSY the U125/1-PGM. End-stations were employed that included facilities for photoelectron energy analysis by means of a hemispherical electrostatic analyser and surface structural characterisation using low-energy electron diffraction (LEED). In the case of the x-ray absorption measurements, the absorption coefficient was monitored indirectly via the total electron yield measured either by means of the sample drain current or using a channeltron-based detector mounted in the analysis chamber. The overall energy resolution and other pertinent parameters will be given in the appropriate figure captions.

Fig. 1a–e Schematic representation of the high-energy spectroscopies used in the investigations of endohedral fullerenes presented here. Shown are the highest occupied molecular orbitals (grey boxes) and the lowest unoccupied molecular orbitals (white boxes), as well as a core level (black horizontal line). The dark grey circles represent electrons and the white circles holes. N, N+1 or N-1 refer to the number of electrons in the system in the final state (initial state= N electrons). The different panels represent: a valence band photoemission, b core-level photoemission, c x-ray absorption, d resonant photoemission (here the participator channel) and e an interband transition in an electron-energy-loss experiment, where the black circle and horizontal arrow represent the primary electron beam.
2.2.3
**Electron-Energy-Loss Spectroscopy**

The electron-energy-loss spectroscopy (EELS) was performed in transmission with a primary beam energy of 170 keV in a purpose-built UHV spectrometer described in detail elsewhere [5]. For the valence level excitations and elastic scattering (electron diffraction) data the momentum resolution of the instrument was set to 0.04 Å⁻¹ with an energy resolution of 90–140 meV. The core level excitations were performed with a momentum and energy resolution of 0.2 Å⁻¹ and 90–140 meV, respectively. All EELS experiments were conducted at room temperature.

3
**Results and Discussion**

3.1
**Monometallofullerenes**

The first endohedral fullerenes to be studied in detail are the monometallofullerenes, with the general formula M@C\(_n\). Until the recent synthetic breakthroughs as regards the trimetal nitride endohedrals [6], monometallofullerenes of the rare-earth metals such as M@C\(_{82}\) were the most abundant endohedral fullerenes and have been the subject of numerous investigations worldwide.

3.1.1
**Gd@C\(_{82}\)**

Considering the encapsulated nature of the metal ion(s) inside the fullerene cage of an endohedral, the most natural and important question to pose is that of the degree of charge transfer between the metal ion(s) and the host cage. Figure 2 shows valence band photoemission profiles of the higher fullerene C\(_{82}\) and that of a typical rare-earth monometallofullerene, Gd@C\(_{82}\) [7], recorded with He:λ\(_{\alpha}\) radiation. These spectra reflect the occupied electronic states of the endohedral fullerene having C 2s and C 2p character, i.e. they show the occupied \(\sigma\) and \(\pi\) molecular orbitals (MO's). Considering first the structures visible above 5 eV binding energy, we note that these MO's – mainly attributable to \(\sigma\)-states responsible for the bonding framework of the C\(_{82}\) cage – are not strongly perturbed by the inclusion of the Gd ion in the centre of the fullerene. Having said that, in La@C\(_{82}\), a scaled C\(_{82}\) spectrum was subtracted from that of the endohedral [8], and small changes in the \(\sigma\)-MO distribution were concluded, indicating that there can be a non-zero degree of hybridisation between the encapsulated metal ion and the fullerene cage states across a fairly wide energy range.

The differences between the endohedral and empty fullerene are much greater for binding energies below 5 eV, i.e. for the \(\pi\)-MO's. The most striking alteration is the population of MOs below 1 eV which were formerly unoccupied in the empty fullerene. This points to a transfer of charge from the Gd ion to low-lying
The electronic states of the carbon cage to form a molecular salt, Gd\textsuperscript{x+}@C\textsubscript{82}. The stability of the 4f\textsuperscript{7}, half-filled shell configuration means that Gd behaves as the epitome of a trivalent rare-earth ion. Thus, within an ionic picture for the charge transfer, one would expect a 3+ Gd ion encapsulated within a (C\textsubscript{82})\textsuperscript{3–} fullerene cage. However, from the valence band photoemission spectra of the carbon MO’s as shown in Fig. 2, it is not feasible to try and answer the question as to whether the Gd ion is truly 3+ and has thus transferred three electrons to the carbon cage. The one statement that one can make – although here the reader will have to accept a comparison with photoemission data from other metallofullerenes (such as Tm@C\textsubscript{82}) which will be presented later in the chapter – is that the low-lying spectral weight seen in the blow-up of the endohedral spectrum shown in the inset to Fig. 2 is not incompatible with the existence of a SOMO (singly occupied molecular orbital) in the Gd@C\textsubscript{82} system.

A more direct probe of the Gd valence is offered by spectroscopies involving the core electrons of the rare-earth ion. In this context, due to their compact nature and reclusive character as far as chemical interaction is concerned, we include the 4f shell in the description ‘core level’.

Figure 3a shows photoemission data from a Gd@C\textsubscript{82} [7] film measured with Al:K\alpha x-rays compared to the ‘empty’ fullerene C\textsubscript{82}. Even at a glance it is easy to see that the x-ray photoemission spectrum of Fig. 3a differs strongly from that shown in Fig. 2: now the C 2s/2p-derived \( \sigma \) and \( \pi \) MO’s are much less distinct and the spectrum is dominated by a large structure centred at a binding energy of about 11 eV. The C\textsubscript{82} spectrum can be taken as a good approximation for the C 2s/2p contribution to the photoemission spectrum, and thus can be used to subtract the non-Gd related emission, resulting in the spectrum shown in Fig. 3b. This ‘pure’ Gd emission can then be simulated using a simple atomic multiplet.

**Fig. 2** Valence band photoemission profiles of ‘empty’ C\textsubscript{82} and Gd@C\textsubscript{82}, recorded at room temperature with He:I\alpha (21.22 eV) radiation. The inset shows the region close to the Fermi level on an expanded scale. For this photon energy, the photoionisation cross sections of the C 2s and C 2p levels dominate that of the Gd 4f levels.
Fig. 3  a Valence band spectra of Gd@C_{82} (grey) and C_{82} (black) measured with Al:Kα x-rays. b Symbols: Gd 4f photoemission after subtraction of the 'empty' C_{82} C 2s/2p spectrum. The vertical lines are individual components of atomic calculations for a 4f^6 multiplet, and the solid curve is their broadened sum. c Gd–N_{4,5} x-ray absorption spectrum (Gd 4d–4f excitations) of Gd@C_{82}. The complex lineshape comes from the widely spaced multiplet components resulting from the strong Coulomb interaction between the single hole in the 4d shell and the eight electrons present in the 4f shell in the x-ray absorption final state [see Fig. 1c]. The arrows represent the two photon energies used for the data shown in panel d. d Resonant photoemission data of the valence band region of Gd@C_{82} recorded ‘off’ (hν=137 eV) and ‘on’ (hν=149 eV) the Gd 4d–4f ‘giant’ resonance
calculation [9]. Here the solid vertical lines in Fig. 3b show the individual components of a $4f^6$ multiplet manifold, and the overall spectrum can be well fitted using a broadened sum of these individual multiplet final states. Bearing in mind that photoemission results in an $N-1$ final state\(^1\) (see Fig. 1a), the excellent agreement of the $4f^6$ multiplet with the $4f$ photoemission data is clear evidence for a $4f^7$ Gd configuration in the initial state. Thus, the Gd $4f$ occupancy would appear to confirm the idea of an encapsulated Gd$^{3+}$ inferred from the He:I$\alpha$ valence band data. However, with reference to the case of La@C\(_{82}\) [10] – in which resonant photoemission was used to illustrate that there was still a finite occupation of the La 5d shell (estimated as roughly 1/3 of an electron) – before we can make any statement concerning the charge state of the Gd ion and thus the effective charge transfer to the carbon cage, we need to consider the Gd’s valence electrons, and in particular the 5d electrons. A first hint that the 5d shell is not significantly occupied is given by the ‘Gd-only’ data shown in Fig. 3b. Here, apart from the large 4f-derived feature, there is little or no structure at energies closer to the Fermi level.

Figure 3c shows the x-ray absorption spectrum of Gd@C\(_{82}\) recorded at the Gd-N\(_{4,5}\) edge (i.e. representing the spectrum of possible transitions between the Gd 4d and 4f shells). It is evident that the lineshape here – resulting from the manifold of different ways in which the 4d core hole and the six 4f holes (the $N+1$ final state has a $4f^8$ configuration) can be arranged – is a complex one. For our purposes, it suffices to say that the main feature located at ca. 148–149 eV corresponds to Gd in a $4f^7$ initial state configuration.

In order to be even more certain as regards the possible occupation of the Gd 5d levels, one should examine photoemission data recorded at either the 3d–4f or 4d–4f resonances, as ‘on resonance’ any 5d character in the valence band can become highly apparent due to resonant enhancement of the photoionisation cross section for states of this atomic character. The x-ray absorption spectrum of Fig. 3c gives us a guide to the photon energies to choose in a resonant photoemission experiment. The downward-pointing arrow in Fig. 3c indicates the ‘off resonance’ value of 137 eV, while the upward-pointing arrow indicates an ‘on resonance’ value of 149 eV. The resonant photoemission data are shown in Fig. 3d. On resonance, the photoionisation cross section for the Gd 4f emission is enormously enhanced, as is clearly seen in Fig. 3d. As a first point, this resonant behaviour serves to confirm the Gd 4f identity of the 11 eV structure. The fact that no significant intensity variations are observed for states with binding energies below 5 eV could be taken as signalling that these $\pi$-MO’s only have at most a very small admixture of Gd 5d character. However, one should bear in mind that the degree to which the emission related to the Gd 5d-related states should be enhanced on resonance will not necessarily be the same as in resonant photoemission data from, for example, La@C\(_{82}\) [10] recorded at the M\(_{4,5}\) edge. The degree of resonant enhancement of the Gd 4f emission ‘on resonance’ in the

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\(^1\) Photoemission from the 4f levels of the rare-earth metals and their compounds provides a clear example of a situation in which the ‘$N-1$’ nature of the photoemission final state needs to be explicitly taken into account to give a correct interpretation of the data.
endohedral is significantly less than in metallic gadolinium, suggesting that there is indeed a non-zero degree of additional hybridisation in the endohedral between the Gd valence states (e.g. 5d) and in this case the carbon 2s/2p states of the C\(_{82}\) cage, leading to the reduction in the lifetime of the intermediate state in the resonant photoemission process and thus a weaker resonant enhancement. Consideration of this fact, together with the strong similarity between the energy distributions of the \(\pi\)-MOs of Gd@C\(_{82}\) and La@C\(_{82}\) [8, 10] leads one to the conclusion that the encapsulated Gd ion is in a 4f\(^7\) initial state configuration (trivalent), with a high degree of charge transfer to give essentially a Gd\(^{3+}\)(C\(_{82}\))\(^{3-}\) molecular salt, but with a finite degree of hybridisation between the MOs of the carbon cage and the valence levels of the encapsulated Gd ion.

Bearing in mind the charge transfer from the encapsulated ion to the carbon cage, endohedral fullerene formation can be considered as an ‘in-ball’ doping of the \(\pi\)-electron system. An endohedral fullerene molecule such as Gd@C\(_{82}\) condenses into a solid structure quite like the fcc/simple cubic structure of solid C\(_{60}\), and thus offers the possibility of intercalation with alkali metals in order to carry out further doping of the low-lying \(\pi\)-MO’s. We have explored this possibility in the case of K\(_x\)Gd@C\(_{82}\), measuring the valence band photoemission and K 2p/C 1s core level signals as a function of K content. Later in the chapter data will be presented for an analogous ‘combinational’ doping in K\(_x\)Tm@C\(_{82}\); at this stage it suffices to say that the K-intercalated Gd@C\(_{82}\) system did not exhibit any alteration of the Gd 4f electron occupation, nor any signs of either metallic behaviour (no Fermi edge visible for any doping level) or separation into different intercalated phases.

### 3.1.2 Tm@C\(_{82}\)

The previous section showed that even the novel surroundings of the interior of a fullerene molecule surrounded by interstitial K ions were not sufficient to tempt a Gd ion inside the cage, to take on a different charge state than its standard trivalent repertoire. In this section, we turn our attention to a remarkable case in which an endohedral fullerene can boast of being a singular example of an air-stable solid in which Tm ions are present in a purely divalent form.

In this case, Tm endohedrals of different structural isomers of C\(_{82}\) could be separated [11] using HPLC. The two different carbon cages have symmetry C\(_6\)(6) and C\(_3\y\)(8), where the numbers in brackets correspond to the naming convention given in Ref. [12]. Figure 4 gives a first clue that the situation in the Tm endohedral is radically different to that in the Gd [7] or La [8] case. The figure shows the valence band spectrum of two isomers of Tm@C\(_{82}\) measured with He:1\(\alpha\) radiation. As was the case for ‘empty’ C\(_{76}\) [13], the energetic distribution of the low-lying \(\pi\)-MO’s is a sensitive function of the details of the different cage structures and thus differs for the two isomers. Upon further consideration – and upon comparison with the spectrum of Gd@C\(_{82}\) – the lack of low-lying spectral weight in the Tm case, as well as the relatively large binding energy of the onset of valence band emission, would suggest that neither of the Tm@C\(_{82}\) isomers supports a SOMO [14, 15]. Considering that two electrons can be accommodated
in each of C$_{82}$’s MO’s, this would suggest either a divalent or tetravalent state for the Tm ions.

Once again, a more definitive statement is possible as regards the Tm valence and the charge transfer to the fullerene cage on the basis of core-level spectroscopic data. Figure 5 shows (a) the valence band spectra of Tm metal and Tm@C$_{82}$, recorded using Al:K$_\alpha$ radiation, together with (b) the Tm 4d–4f excitation spectra of the same systems [15]. Taking first the uppermost pair of spectra, in Tm metal both the 4f photoemission lineshape and the Tm-N$_{4,5}$ core-level excitation spectrum are indicative of the 4f$^{12}$ initial-state configuration characteristic of trivalent thulium. In particular, the multiplet manifold predicted from atomic multiplet theory [9] agrees excellently with the experimental 4f photoemission profile.

Turning now to the spectra of the endohedral in the lower parts of Fig. 5a,b, one immediately recognises a completely different situation. Now the multiplet ‘fingerprint’ of the 4f photoemission agrees perfectly with the atomic multiplet distribution for a 4f$^{12}$ final state (i.e. 4f$^{13}$ initial state), and the single component character of the Tm-4d excitation spectrum is also fully consistent with the lack of multiplet structure expected for a 4f$^{14}$ final state (i.e. 4f$^{13}$ initial state). Thus, from the core-level spectroscopic data of Tm@C$_{82}$, the Tm4f electron count is determined to be 4f$^{12}$, indicating that the thulium is divalent in this system. This, in turn, is consistent with the lack of a SOMO in the He:I$\alpha$ valence band photoemission data shown in Fig. 4.

As has been pointed out for the case of La@C$_{82}$ [10] and mentioned above, hybridisation between the valence levels of the lanthanoid and the $\pi$-MO’s of the fullerene cage can result in non-zero population of the metal ion’s 5d/6s levels. In our case, any residual Tm 5d occupancy due to hybridisation would – in combination with the 4f$^{12}$ initial state determined from the data of Fig. 5 – mean that
the effective valency of the Tm ions is less than divalent. Figure 6 shows valence band photoemission spectra of Tm@C82 recorded for photon energies crossing the Tm 4d–4f excitation threshold, as shown in the inset containing the Tm-N4,5 x-ray absorption spectrum of the system.

It is clear from the figure that the 4f multiplet structure is enhanced for photon energies at or above the 4d–4f absorption threshold. There are no signs of new spectral structures becoming visible at resonance, indicating that there is insignificant hybridisation between the Tm ion’s valence levels and those of the carbon cage, making the effective valency of the Tm ions precisely two.

With respect to the infamous sensitivity of rare-earth systems to both contamination and deviations in valency due to a reduction in coordination at the surface, we note at this stage that the encapsulated nature of the rare-earth ion brings with it two advantages: (i) Tm ions in fullerene molecules populating the surface layer of the film ‘feel’ no reduction in coordination, and thus possess exactly the same valency as those in the bulk of the film; and (ii) the pure divalent state of the Tm ions is fully protected by the carbon cage, and thus is even unaffected by removal of the film from ultra-high vacuum into air. These two points illustrate the remarkable nature of endohedral fullerenes, and confirm that this system is more suitable than other Tm-containing compounds investigated to date [17] to be considered as the archetypical divalent Tm system.

As regards the comparison between the two endohedrals considered thus far, one is tempted to suggest that the stability inferred by a closed-shell fullerene
electronic configuration is sufficient to drive the Tm into a purely divalent state, whereas the special stability of the 4f7 configuration ensures that Gd remains trivalent, even at the expense of single occupation of the frontier MO of the endohedral.

Figure 7 shows spectra from the Cs(6) isomer of Tm@C82 during a series of experiments in which the endohedral solid was progressively intercalated with potassium as an electron donor to give Kx(Tm@C82) [18]. The left-hand panel shows data recorded using Al:Kα radiation in the region of the C 1s and K 2p core levels. The relative K 2p:C 1s intensity enables an estimate of the appropriate intercalation or x values to be made. From the core-level spectra, even though the intercalation was not carried out using the distillation method [19], there are clear signs of K ions occupying different crystallographic sites of the solid Tm@C82 structure. This can be seen in the presence of a pair of K 2p doublets, one related to K in sites akin to the octahedral sites of a fullerene fcc lattice (higher binding energy), and the other to K in sites akin to the tetrahedral sites (lower binding energy) [20]. In fact, despite the lower symmetry of the carbon cage, the picture that emerges from the intercalation of the endohedral is remarkably similar to that for KxC60 at room temperature for samples prepared in a similar manner [21]. For x<3, the K 2p intensity as a whole grows with x, but the ratio of the tetrahedral:octahedral K 2p component remains 2:1, whereas, for x≥4, only tetrahedrally co-ordinated K ions are found. This would indicate a switch from an fcc-like structure for x<3 to a bct/bcc-like structure for x>4. As in the KxC60 system, the intercalation stops at the level of x=6.

Figure 7b shows valence band photoemission spectra recorded with He:Iα radiation from the Kx(Tm@C82) system. On K doping up to x=2, a new low-energy structure grows in intensity: this is the former LUMO (lowest unoccupied mole-
cular orbital) of Tm@C_{82} which is now filled with up to two electrons transferred from the K4s orbitals of the intercalant. For \( x > 2 \) this structure shifts to higher binding energy. For \( 2 < x < 4 \), a second low-energy structure grows before shifting away from \( E_F \), until for \( 4 < x < 6 \), a third previously unoccupied MO is filled in this step-wise manner. By analysing the shifts of the centroids of the LUMOs as they get filled, one can estimate an energy level scheme for the Cs(6) isomer of C_{82} in the endohedral with successive energy separations of 0.85, 0.35 and 0.4 eV between the HOMO, LUMO, LUMO+1 and LUMO+2 molecular levels [18]. This kind of rigid-band-like doping behaviour has not been seen in intercalation compounds of either C_{60}, nor in other combinationally doped metallofullerenes.

In the end in K_{x}(Tm@C_{82}) eight electrons have been transferred to the C_{82} cage by a combination of the endohedral (two electrons from the Tm ion) and exohedral (six electrons from the K ions) doping. At no stage is there any significant emission at the Fermi level, \( E_F \), nor sign of a Fermi edge, indicating that for \( x \) up to 6 in K_{x}(Tm@C_{82}), no metallic phases are formed. The lack of significant changes in the main characteristic of the Tm 4f photoemission data recorded using Al:Kα radiation from the same films (not shown), and the lack of significant changes in Tm-M_{4,5} x-ray absorption data for the K_{x}(Tm@C_{82}) end member of the series (not shown), attests to the fact that – despite the large pool of electrons potentially available to the Tm ion – the encapsulated Tm ion remains steadfastly divalent.
3.1.3

Conclusions: Monometallofullerenes

In this first results section, we have dealt with two monometallofullerenes of C\textsubscript{82} in which either Gd or Tm rare-earth ions are encapsulated in the fullerene cage. The main results can be summarised as follows:

- Gd is trivalent.
- Tm is divalent.
- These valency statements are consistent with the characteristic multiplet structures in 4f photoemission and N\textsubscript{4,5} x-ray absorption, as well as the low-lying distribution of the occupied carbon-derived MO’s.
- In the Tm case, resonant photoemission proves that there is no significant hybridisation between the rare-earth 5d levels and the carbon electronic states; thus the Tm ions have an essentially ionic interaction with their fullerene host.
- In the Gd case, the magnitude of the resonant enhancement of emission from the 4f levels signals the presence of hybridisation between the Gd valence levels and those of the carbon cage. However, this does not alter the conclusion as regards the Gd’s trivalency and the transfer of essentially three electrons to the fullerene MOs.
- The remarkably pure divalent state of Tm in Tm@C\textsubscript{82} is even robust with respect to air exposure.
- Additional electrons can be transferred to the C\textsubscript{82} molecules via alkali-metal intercalation: under standard intercalation conditions, for both systems saturation is reached at six K ions per endohedral fullerene molecule.
- The endohedral fullerene salts thus formed exhibit different interstitial sites upon K intercalation and show signs of phase separation, as was the case in fullerene salts of C\textsubscript{60} and C\textsubscript{70}.
- None of the phases formed upon intercalation shows signs of being metallic. Even upon loading the carbon cage with a total of eight electrons [in the K\textsubscript{6}(M@C\textsubscript{82}) systems], the valency of the encapsulated rare-earth ion is not reduced.

3.2

Dimetallofullerenes

Having now familiarised ourselves with the issues at hand and the high-energy spectroscopic approaches available in the investigation of metallofullerenes, based upon the relatively simple examples of rare-earth monometallofullerene structures, we now move on to endohedrals in which two metal ions are encapsulated, or dimetallofullerenes.

3.2.1

Ce\textsubscript{2}@C\textsubscript{72}

The first dimetallofullerene we consider is also a rare-earth system – Ce\textsubscript{2}@C\textsubscript{72}. Cerium is generally found in the trivalent state with a 4f\textsuperscript{1} configuration, but can also take on a tetravalent state formally with zero population of the 4f shell. If we
assume for the moment that the cerium dimer’s valence electrons (in the 5d and 6s orbitals) would be donated to the fullerene cage in an endohedral, then a pure trivalent Ce would result in transfer of six electrons and tetravalent Ce of eight electrons to the C\textsubscript{72} cage. Thus, it is evident that here – unlike the case of Gd@C\textsubscript{82} vs. Tm@C\textsubscript{82} – the valence band photoemission data of the carbon-derived C\textsubscript{72} molecular orbitals will not be of much assistance, as in both cases a closed-shell fullerene electronic configuration is possible, and no tell-tale SOMO structure would be visible.

In the left panel of Fig. 8, we show x-ray absorption data from Ce\textsubscript{2}@C\textsubscript{72} recorded at the Ce-M\textsubscript{4,5} (mainly Ce 3d → 4f transitions) and Ce-N\textsubscript{4,5} edges. In general, x-ray absorption data from Ce, and in particular at the higher energy L\textsubscript{2,3} edge, has been extensively used to determine Ce valencies within the context of the investigation of cerium’s mixed valent and heavy fermion (Kondo resonance) behaviour in both Ce metal and in Ce compounds [22, 23]. The energetic position and the form of the L\textsubscript{2} and L\textsubscript{3} spectral components [22, 23] are in keeping with an effective (initial state) Ce 4f occupation that is close to one – i.e. the Ce ions are formally trivalent. The right panel of Fig. 8 displays analogous data recorded at the Ce-N\textsubscript{4,5} edge, which is typical of N\textsubscript{4,5} data of light rare earths with a number of weak multiplet lines preceding an asymmetric, so-called giant resonance. For light rare earths, both the higher-energy members of the multiplets and the giant resonance are dominated by ‘tunnelling’-like final states (4d\textsuperscript{4} 4fn\textsuperscript{ef}) [24] in which the photoelectron reaches low kinetic energy continuum states and thus displays a strong material dependence\textsuperscript{2}. The form of the N\textsubscript{4,5} spectrum

\textbf{Fig. 8}  \textit{Left panel:} x-ray absorption spectrum of Ce\textsubscript{2}@C\textsubscript{72} at the Ce-M\textsubscript{4,5} edge. The two main groups of features occur at an energy position characteristic for a 4f\textsuperscript{2} final state, indicative of trivalent Ce. The arrows indicate the typical energy positions for a spectral structure in systems containing tetravalent Ce ions (4f\textsuperscript{1} final state). \textit{Right panel:} x-ray absorption spectrum of Ce\textsubscript{2}@C\textsubscript{72} at the Ce-N\textsubscript{4,5} edge. The numbers show the photon energies used for the resonant photoemission experiments whose data are shown in Fig. 9. For the photon energies indicated with 1 and 5, the value is beyond the energy range shown in the figure.

\textsuperscript{2} Lower-energy multiplets result from super Coster–Kronig and Coster–Kronig decay channels and thus their spectrum is less sensitive to the ‘chemistry’ of the environment [24].
of Ce$_2$@C$_{72}$ shown here is typical for essentially trivalent Ce systems [22]. The numbered arrows superimposed upon the Ce-N$_{4,5}$ spectrum illustrate the position of the photon energies used for resonant photoemission (see below).

Now the question arises, as before, of the degree to which the rare earth's valence electrons (and in particular 5d) are populated by hybridisation with the electron-rich $\pi$-MO system of the C$_{72}$ host molecule. Figure 9 shows resonant photoemission spectra of Ce$_2$@C$_{72}$, with photon energies selected to span the N$_{4,5}$ core level excitation spectrum, as indicated in Fig. 8.

The spectrum plotted in black ($h\nu=123$ eV) is recorded with a photon energy at the maximum of the giant resonance, and shows a clear resonant enhancement of the structure located at just under 1 eV binding energy. States located close to 6 eV binding energy also exhibit greater intensity for $h\nu=123$ eV.

In this case, the fact that a large resonant enhancement is seen of the states at around 1 eV is consistent with the behaviour of other dominantly trivalent Ce-based systems, as it is here that the 4f$^0$ photoemission final-state spectral weight occurs for systems with a 4f$^1$ initial-state configuration. Thus, from the resonant photoemission data, we can confirm the trivalent nature of the Ce ions in Ce$_2$@C$_{72}$ and conclude that there is relatively weak hybridisation between the Ce 5d and the C 2s/2p states of the fullerene cage in this case. A shorthand notation for the cerium dimetallofullerene could thus be (Ce$_2$)$_{6^+}$(C$_{72}$)$_{6^-}$.

From this example, it would appear that even in dimetallofullerenes, the valence levels of rare-earth encapsulants hardly hybridise at all with the carbon states, leading to integer valencies, like three, in the case of Ce$_2$@C$_{72}$. The next class of dimetallofullerenes to be dealt with are those of the transition metals, and these are quite a different story.
3.2.2

Sc$_2$@C$_{84}$

Of the transition-metal metallofullerenes, the Sc-containing systems are of particular interest as they can be synthesised in the form of mono-, di-, tri- and even tetrametallofullerenes [25]. Among the possible transition-metal encapsulates, Sc species also have the advantage that the most common valencies – trivalent and divalent – have the simple initial-state d-counts of d$^0$ and d$^1$. Thus, evidence for population of the Sc 3d shell is already a clear sign that one has moved away from the ‘ionic’ trivalent paradigm seen in all cases so far (with the notable exception of Tm@C$_{82}$).

In this section, we will present and discuss results from Sc$_2$@C$_{84}$, which is the most widely studied dimetallofullerene to date. Early scanning tunnelling microscopy [26] and transmission electron microscopic [27] investigations provided evidence in favour of the endohedral structure of this system, which was later confirmed by x-ray diffraction experiments utilising maximum entropy methods [28]. Before experimental data from this system were available, the Sc ions were predicted to be divalent from quantum chemical calculations [29]. Subsequent data from vibrational spectroscopy [30, 31], core-level photoemission [32] and further theory [33] on this system were indeed interpreted in terms of divalent Sc ions.

In the lower panel of Fig. 10 we show the Sc 2p core-level photoemission spectrum of a UHV-prepared film of Sc$_2$@C$_{84}$ [34]. Analogous data, but from films prepared by dropping from a solvent solution in air, were used in [32] to argue that, as the binding energy of the Sc 2p spin-orbit split components is lower than in Sc$_2$O$_3$ (a trivalent Sc standard), the Sc ions in the endohedral fullerene are divalent.

![Core-level photoemission spectra of (top) Sc$_3$N@C$_{80}$ [36] and (bottom) Sc$_2$@C$_{84}$ [34] recorded using Al:K$\alpha$ radiation](image)
Aware of the fact that the absolute binding energy in core-level photoemission of transition-metal systems can be strongly influenced by screening and charge-transfer effects in the photoemission final state, we turned to x-ray absorption as a highly direct probe of the valency of transition-metal and rare-earth systems [35].

In Fig. 11, we show the Sc-L 2,3 x-ray absorption spectrum of a thin film of Sc$_2$@C$_{84}$ recorded at room temperature. Before comparing the results with simulations based upon atomic multiplet calculations, the experiment was repeated at low temperature (50 K) in order to minimise the effects of phonon-induced broadening, which is not taken into account in the multiplet calculations. The low-temperature data are also shown in Fig. 11. To illustrate the sensitivity of the Sc-L 2,3 spectra to the 3d count (and hence the valency), Fig. 11 includes the results of broadened atomic multiplet calculations for a 2p$^d_1$ and 2p$^d_2$ final state – i.e. corresponding to pure trivalent or divalent Sc, respectively [34]. It is evident from the simulations that the strong Coulomb interaction between the 2p and 3d shell means that the fine structure of the spectra would be expected to be totally different (and thus easily distinguishable) for divalent or trivalent Sc ions. Therefore, this experiment is a much more suitable probe of the Sc valency than x-ray photoelectron spectroscopy [32] or vibrational spectroscopy [30, 31], the latter of which only allows application of a severely simplified force constant model in order to give indirect information regarding the charge state of the encapsulated Sc dimer.

As regards the x-ray absorption data themselves, it is evident from the low-temperature spectrum in Fig. 11 that the broad ‘wings’ of the main spin-orbit split components are unlikely to be of vibronic origin. It is equally clear that the data do not fit the expectations for divalent Sc ions, thus illustrating that extreme caution is needed in simply ‘reading off’ the valency from the Sc 2p core-level
binding energy [32], or in using indirect methods based on the dynamics of the Sc cluster/carbon cage vibrational modes [30, 31] to estimate the Sc valency.

Thus, were one merely to conclude from the better agreement with the 2p\(d^1\) final state simulation that the Sc ions are trivalent, adopting an ionic picture, one would arrive at a charge balance, \((\text{Sc}_2)^{6+}(\text{C}_{84})^{6–}\). Having said that, the prediction for fully ionic Sc\(^{3+}\) ions in Fig. 11 also does not fit the experimental spectrum exactly, neither in terms of the extra width seen in experiment, nor as regards the branching ratio between the \(L_2\) and \(L_3\) parts of the spectrum [34]. Consequently, in order to determine the true effective valency in this case with a good degree of security, it is necessary to carry out a more detailed theoretical analysis of the data.

In general, one method to go beyond pure ionic configurations in the simulation of x-ray absorption spectra of transition-metal compounds is to include the effects of charge transfer. In this context, this would mean consideration of initial states with an admixture of other configurations due to charge transfer between the fullerene cage and the Sc ions. Thus, rather than, say, having only a 3d\(^0\) initial state configuration, there is an admixture of 3d\(^{n+1}\)\(L\) initial states, where the \(L\) denotes a hole located in the ligand (fullerene) electronic states. In our case, this means that rather than only a pure ‘ionic’ 3d\(^0\) Sc\(^{3+}\) initial-state configuration, we have an admixture of \(N\%\) 3d\(^1\)\(L\) initial-state character. For details of the calculation, the reader is referred to Ref. [34]. It is sufficient here to state that the charge-transfer energy in the initial (final) state was taken to be 2 (0) eV, and that the hopping term (which gives a measure of the hybridisation between the C 2p and Sc 3d orbitals) used was 1 eV [34].

In these charge-transfer atomic multiplet calculations, the effective formal valency of the encaged Sc ions is given by the ratio of the d\(^0\) and d\(^1\) initial-state contributions, which represent trivalent and divalent Sc, respectively. Figure 12 shows how the spectrum would evolve from the pure d\(^0\) initial state.

Fig. 12 Simulated Sc-L\(_{2,3}\) x-ray absorption spectra of trivalent Sc ions (d\(^0\)) with an initial state admixture of the indicated proportion of a d\(^1\)\(L\) configuration in the initial state. For details of the calculations, see Ref. [34]
(i.e. \( \text{Sc}^{3+} \): the same as the bottom-most spectrum in Fig. 11) through to a pure \( \text{d}^1 \) initial state (i.e. \( \text{Sc}^{2+} \): the same as the top-most spectrum in Fig. 11). As the proportion of the \( \text{d}^1 \text{L} \) admixture increases, not only does the width of the main multiplet components increase, but also new spectral weight grows at ca. 404 eV and also at energies above 408 eV.

The fact that there are no clearly resolved features at either 404 or above 408 eV in the experimental spectrum, as well as the observed branching ratio, puts an upper limit on the \( \text{d}^1 \text{L} \) admixture. A direct comparison of the best fit between the simulation and the low-temperature experimental spectrum is shown in Fig. 13. The choice of 39\% admixture of \( \text{d}^1 \text{L} \) states results in the best match as regards both the overall shape of the spectrum and the branching ratio\(^3\). This results in a 3d electron count in the initial state of 0.39, or an effective valency of 2.61. Thus, although the Sc ions are in a dominantly trivalent state [Sc(III)], there is significant hybridisation between the Sc states and those of the carbon cage\(^4\), meaning that this example goes well beyond the largely ionic interactions we have seen in a number of the examples up to now, making this system reminiscent of the situation proposed for the monometallofullerene La@C\(_{82}\) [10].

With this example of data from the dimetallofullerene \( \text{Sc}_2@C_{84} \), the efficacy of combining x-ray absorption and charge-transfer atomic multiplet calculations in investigating the valency, charge transfer and cage–metal interaction of more complex, hybridised systems such as \( \text{Sc}_2@C_{84} \) has been demonstrated. Based on the valence sensitivity of the measurement, we are confident in overruling

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\(^3\) Still better agreement could be expected (in particular in terms of the observed width of the features) if the non-spherical nature of the \( C_{84} \) cage, the off-centre position of the Sc ions and the non-rectangular shape of the C 2p-based hybridisation band were to be taken into account [34].

\(^4\) Given the large Sc–Sc distance of 3.9 Å in this system [28], Sc–C hybridisation is more likely than Sc–Sc hybridisation.
interpetations of experiments possessing significantly less direct access to the valence of the Sc ions [28, 30–32]. We determine the Sc ions in this system to be trivalent, but do find that the Sc ions exhibit significant hybridisation with the C 2p states, resulting in an effective d electron count of 0.39 per Sc ion.

To close this section, we mention that after the combined x-ray absorption and theoretical investigation of Sc₂@C₈₂ discussed here was published [34], transmission electron microscopic measurements of single Sc₂@C₈₄ molecules which are themselves encapsulated inside carbon nanotubes (forming a so-called peapod) have been interpreted in terms of divalent Sc ions in this system [37]. While the ‘observation’ of the Sc ions using electron energy-loss contrast at a single-ion level is undoubtedly a tour de force as regards microscopy, the interpretation of the Sc-L₂,₃ excitation edges presented in the paper ignores the vital physics of the final-state multiplet structure which is so necessary for a correct interpretation of such core-level excitation data from transition-metal species. Thus, until a complete theoretical treatment of the data of Ref. [37] is presented (at least at the level of the charge-transfer atomic multiplet approach presented here), which gives a firm foundation to the claim of the divalent nature of the Sc ions of individual Sc₂@C₈₄ molecules in the electron beam, the defining results and conclusion for the Sc₂@C₈₄ system remain those presented here and in Ref. [34].

3.2.3 Conclusions: Dimetallofullerenes

In this second results section, we have dealt with two examples of dimetallofullerenes: Ce₂@C₇₂ and Sc₂@C₈₄. The main results can be summarised as follows:

– From the analysis of x-ray absorption spectra at the Ce-M₄,₅ and -N₄,₅ edges it is clear that Ce in Ce₂@C₇₂ is trivalent (4f¹ initial state configuration).
– Resonant photoemission at the Ce 4d edge shows the Ce valence electrons to be practically fully ionised, leading to a shorthand for this molecule of (Ce₂)⁶⁺@(C₇₂)⁶⁻.
– The low level of hybridisation between the Ce valence levels and the MO’s of the C₇₆ host molecule indicates a high level of ionic character for the Ce–C₇₆ interaction in this system.
– Sc in Sc₂@C₈₄ has the form of trivalent Sc(III) ions.
– As regards the interactions between the encaged metal ions and the host cage, the Sc₂@C₈₄ system presents a very different picture to the Ce₂@C₇₂ case. In Sc₂@C₈₄ the fine structure and branching ratio in the Sc-L₂,₃ x-ray absorption spectra require a strong hybridisation between the 3d levels of the Sc ions and carbon-derived MO’s of the C₈₄ molecules.
– Simulation of the data within the framework of charge-transfer atomic multiplet calculations shows that this hybridisation yields an effective Sc 3d electron count of about 0.4 electrons, or a valency of 2.6.

5 The reduction of transition-metal species under the intense electron irradiation of the high-resolution electron microscope used in [37] additionally represents a process that could also lead to Sc-L₂,₃ data deviating from those presented here, which were measured with the ‘gentle’ method of soft x-ray absorption.
3.3
Endohedral Fullerenes Containing Metal Nitride Units

In this last results and discussion section of the chapter, we move on to another member of the Sc endohedral family and deal with the trimetal nitride, endohedral Sc$_3$N@C$_{80}$. This system has become the focus of quite some research attention, both from the point of view of its synthesis as well as with regards to its electronic structure and bonding properties.

From the synthetic point of view this is a representative of a remarkable family of metal nitride endohedrals, A$_x$B$_{3x}$N@C$_{80}$ ($x=0$–3), which, under the right conditions, can become the main product in the Krätschmer–Huffman carbon arc-based synthesis, rather than being present at low level as a ‘by-product’ of C$_{60}$ and C$_{70}$ synthesis [6, 38].

The $^{13}$C NMR spectrum of Sc$_3$N@C$_{80}$ has only two lines, consistent with $I_h$ symmetry for the fullerene cage [6], which has excited much interest not only because it would be the first $I_h$ fullerene to be isolated in significant quantities after C$_{60}$, but also because of the fact that ‘empty’ C$_{80}$ has $D_2$ symmetry [39]. Calculations dealing with the seven structural isomers of C$_{80}$ that obey the isolated pentagon rule have predicted that going from the neutral to a C$_{80}^-$/state, the icosahedral C$_{80}$ would switch from being the least stable to the most stable carbon cage [40] and that this $I_h$ structure could become even more energetically favourable in the C$_{80}^{2−}$/state [40–42]. Therefore it seems natural to suggest that the C$_{80}$ cage with $I_h$ symmetry is stabilised by charge transfer from the nitride cluster in Sc$_3$N@C$_{80}$. The exact amount of charge transfer is of interest and should be determined experimentally, not only to settle this specific question, but also to further our knowledge of these novel encapsulated transition-metal-nitride fullerene clusters in general.

Returning to Fig. 10, we see from the top spectrum that the binding energy of the Sc 2p core level photoemission features is no different than it was in Sc$_2$@C$_{84}$. At lower binding energy, the N1s signal of the trimetal nitride cluster is observed. As a result of our experience gained with the Sc$_2$@C$_{84}$ system, we refrain from trying to attach a ‘valency’ interpretation to the absolute binding energy position of any of the peaks in the core-level photoemission data. Consequently, we turn straight away to Sc-L$_{2,3}$ x-ray absorption, in conjunction with charge-transfer atomic multiplet calculations [36] (Fig. 14).

As was the case in the Sc dimetallofullerene, the charge-transfer atomic multiplet calculations are well suited to simulate the experimental core excitation spectrum to a good degree of accuracy. In the case of Sc$_3$N@C$_{80}$, the experimental spectrum obviously does not match either of the extreme (d$^0$ or d$^1L$) configurations but rather lies in between. This indicates that hybridisation effects have to be taken into account. In fact a d$^1L$ admixture of 60% is required for a good fit, both in terms of spectral shape and the branching ratio between the L$_2$ and L$_3$ edges. A 60% d$^1L$ admixture leads to an effective degree of ionisation of close to 2.4 electrons per Sc – i.e. a formal Sc 3d electron count of 0.6 per Sc. This result shows that the valence state of the Sc atoms in Sc$_3$N@C$_{80}$ (3d$^{0.6}$) is reduced as compared to that in Sc$_2$@C$_{84}$ (3d$^{0.4}$), which is consistent with the existence of significant intra-cluster interactions within the Sc$_3$N unit compared to the loosely bound Sc ions in Sc$_2$@C$_{84}$ [43].
The question now arises as to the charge distribution and bonding within the Sc$_3$N cluster. In a naive, ionic picture each Sc could donate one electron to the N (which then has the same closed-shell configuration as neon). The remaining two electrons per Sc could then be transferred to the fullerene cage to give the C$_{80}^{6-}$ required for optimal stability of the icosahedral structural isomer [41, 42]. This scenario would seem to satisfy all requirements with the major exception that the Sc-L$_{2,3}$ x-ray absorption data above clearly point to a Sc d electron count of 0.6, not of zero. The key here is to take the short Sc–N bond length into account (1.98 Å in the endohedral vs. 2.25 Å in bulk ScN [44]). As ScN is quite an ionic compound, the shorter Sc–N distance in the endofullerene is a signal of significant Sc/N covalence. This sharing of electron density will naturally lead to increased charge density at the Sc, thus accounting for the 3d$^{0.6}$ configuration of the Sc ions. This hypothesis receives support from the planar (i.e. not ammonia-like) form of the Sc$_3$N cluster, which is consistent with a significant p$_\pi$–d$_\pi$ (‘back-donation’) component in the Sc–N bonding [43], in which only 0.3 electrons per Sc are fully transferred to N.

Summarising, as a result of the observed formal Sc 3d$^{0.6}$ configuration in Sc$_3$N@C$_{80}$, and based on the foregoing discussion of the Sc–N bonding, one can conclude that (3×2.4)–(3×0.3)=6.3 electrons are available for transfer from a Sc$_3$N cluster on its encapsulation in a C$_{80}$ molecule, thus providing the six electrons required to optimally stabilise the I$_h$ C$_{80}$ cage as discussed above [36].

Having determined that it is very likely that six electrons are transferred to the C$_{80}$ molecule – in agreement with the $^{13}$C NMR data which suggest I$_h$ symmetry for the carbon cage [6] – it is now interesting to consider the valence band photoemission spectrum of the endohedral to see if the consequences of this high symmetry are visible in the energy distribution of the $\pi$-MO’s of the system.

![Simulated Sc-L$_{2,3}$ x-ray absorption spectra of trivalent Sc ions (d$^0$) with an initial-state admixture of the indicated proportion of a d$^1$L$_{2,3}$ configuration in the initial state.](image1.png)

**Fig. 14** Solid lines: simulated Sc-L$_{2,3}$ x-ray absorption spectra of trivalent Sc ions (d$^0$) with an initial-state admixture of the indicated proportion of a d$^1$L$_{2,3}$ configuration in the initial state. For details of the calculations, see Ref. [36]. Line+symbols: experimental Sc-L$_{2,3}$ x-ray absorption spectrum of Sc$_3$N@C$_{80}$.
The He:I\(\alpha\) photoemission spectra shown in Fig. 15 are mainly due to emission from the carbon cage states, bearing in mind the photoionisation cross section for the C 2p, Sc 3d and N 2p levels leads to an upper limit for the contribution from the Sc3N unit to the overall photoemission response upon using He:I\(\alpha\) radiation of only about 2%. Generally, the valence bands of higher fullerenes and metallofullerenes display broad structures in photoemission (see for example Figs. 2 and 5), this breadth reflecting the splitting of electronic states due to the (generally) low symmetry of the carbon cage and due to covalent interactions (hybridisation) between the encaged metal and the host molecule. As typical examples, the spectra of Sc2@C84 and C84 are also depicted in Fig. 15.

In contrast, Sc3N@C80 exhibits four narrow peaks in the low-energy region (binding energy <5 eV) of its valence band photoemission spectrum. This would be fully consistent with the suggestion that the carbon cage possesses high, icosahedral symmetry, with the spectrum of Sc3N@C80 being more comparable to that of C60 (I\(h\)) than to that of pristine C80 (D\(2\)) – a consequence of the high effective degeneracy of the electronic states, concomitant with I\(h\) symmetry of the fullerene cage\(^6\). In addition to the tight bunching of the electronic states of the endohedral in energy, it is also of interest that the onset of the highest occupied molecular orbital (HOMO) is at the relatively large binding energy of ca. 1 eV. The strong electron correlation effects in the fullerenes [45] mean that, in an ionising spectroscopy such as photoemission, this onset energy cannot necessarily be interpreted simply as an expression of the minimal energetic separation of the

\(^6\) The fact that the Sc3N@C80 molecule as a whole has only C\(3\) symmetry (or even is reduced to C\(1\) in the solid state [43]) does not give rise to a lifting of the degeneracy of C80’s molecular orbitals visible above the vibronic broadening, which dominates the width of the individual molecular orbitals in valence band photoemission.
HOMO and LUMO. Nevertheless, the binding energy of this onset is too large to be consistent with an odd-electron system, such as is approximated in certain endohedrals such as M@C_{82} [M=Gd (see Fig. 2) or La]. The onset energy is also such that it presents a strong argument in favour of a \((C_{80})^6^-\) scenario in Sc_{3}N@C_{80}, as the further Jahn–Teller splitting of a three-fold degenerate LUMO (such as that of the C_{80} molecule [40–42]) containing four electrons would not be able to account for the magnitude of the observed gap in the electronic excitation spectrum, whereas a six-fold electron transfer to the \(I_h\) C_{80} cage would result in a closed-shell structure with the excitation gap then corresponding to a large extent to the (large) LUMO–LUMO+1 energy separation. We note that the theoretical predictions of an energy gap of about 2 eV for both \((C_{80})^6^-\) and Sc_{3}N@C_{80} are in qualitative agreement with our observation [42, 43].

To close this section on trimetal nitride endohedral fullerenes, we present and discuss data from potassium intercalation experiments on Sc_{3}N@C_{80}. As was the case for K_{x}(Tm@C_{82}), x-ray photoemission measurements of the K 2p and C 1s signals can be used to give a good indication of the overall potassium concentration in such intercalation compounds. Figure 16 displays the K 2p photoemission lines for several intercalation levels in K_{x}(Sc_{3}N@C_{80}).

As was discussed already in the case of K_{x}(Tm@C_{82}), the existence of pairs of doublets in the K 2p spectra indicates that the metallofullerene crystallises at room temperature in an fcc-like close-packed structure, with both octahedral and tetrahedral interstitial sites serving as hosts for the K ions (respectively labelled O and T in Fig. 16). For an average stoichiometry K_{0.7}(Sc_{3}N@C_{80}), both tetrahedral and octahedral sites are occupied but the latter site is favoured (see bottommost spectrum of Fig. 16), which, bearing in mind the 2:1 T:O ratio mostly seen for \(x=3\) phases, suggests the presence of a K(Sc_{3}N@C_{80}) phase. Upon further intercalation, the O site feature reduces in intensity with respect to the T peak,
consistent with the formation of an fcc-like $K_3(Sc_3N@C_{80})$ phase. Only for higher doping $x>3$ does a transformation into a body-centred structure appear to occur, as signalled by the observation of a new K 2p doublet (marked as $T_2$ in Fig. 16) related to a body-centred crystal symmetry. This is consistent with the formation of a stable phase $K_4(Sc_3N@C_{80})$ or $K_6(Sc_3N@C_{80})$. The Sc 2p and N 1s core-level peaks barely alter at all upon K intercalation (not shown). Likewise, x-ray absorption data recorded at the Sc-M4,5 edge (not shown) also exhibit no changes of the lineshape and of the peak intensities upon intercalation. This makes it clear that the effective Sc valency is not altered with intercalation-induced doping of the metallofullerene, which is in line with intercalation experiments on other metallofullerenes such as those on Gd@C_{82} and Tm@C_{82} [18] discussed above.

The valence band photoemission spectra recorded at various K intercalation levels are presented in Fig. 17. At very low doping, the Fermi level can be assumed to be pinned near the edge of the LUMO, thus making the onset observed at 1.1 eV a more accurate estimation of the bandgap relevant for ionisation of the molecule (second spectrum from the bottom). From $x=0.7$ and upwards, filling of the LUMO gives rise to a broad structure at about 1.5 eV binding energy. Subsequent doping leads to the appearance of several $K_x(Sc_3N@C_{80})$ phases, with the superposition of their different photoemission signatures giving rise to broad spectral structures. The step-by-step intercalation behaviour seen in Fig. 7 for $K_x(Tm@C_{82})$ does not appear to take place in intercalated samples of the triscandium nitride endohedral as prepared here. A consequence of this is that the very sharp peaks observed near the Fermi level in the pristine material merge into structureless features in the valence band of the intercalated material. As has been the case in all intercalation-doped metallofullerenes to date, there is no sign of metallic behaviour in the $K_x(Sc_3N@C_{80})$ system, which spans charge states of the C_{80} cage from 6– ($x=0$) to ca. 11– ($x=5$).
3.3.1 Conclusions: Sc$_3$N@C$_{80}$

In this final results section, we have dealt with a representative of the new class of metallofullerenes containing trimetal nitride clusters: Sc$_3$N@C$_{80}$. The main results can be summarised as follows:

- A significant degree of d$_n$-$p_n$ covalent ‘back-bonding’ within the strongly covalently bound Sc$_3$N unit leads to the presence of a finite 3d electron density at the Sc site, whereby the effective 3d electron count at the Sc sites is 0.6 electrons (compared to a Sc 3d$^{0.4}$ configuration in Sc$_2$@C$_{84}$).
- The Sc$_3$N unit’s remaining six valence electrons are transferred from the encapsulated cluster to the C$_{80}$ cage to give a hexa-anion.
- Although neutral C$_{80}$ is formed as the isomer with $D_2$ symmetry, the Sc$_3$N encapsulation and resultant charge transfer to form the C$_{80}$ hexa-anion makes the endohedral C$_{80}$ molecule stable in the form of the highly symmetrical $I_h$ C$_{80}$ structural isomer.
- This high symmetry results in the close grouping of the $\pi$-MOs and the large binding energy of the valence band onset seen in the photoemission spectrum of the system.
- By analysing the evolution of the K 2p core-level photoemission features as a function of intercalation in K$_x$(Sc$_3$N@C$_{80}$), evidence for the formation of $x=1$, $x=3$ and $x=4$ or 6 phases in the K$_x$(Sc$_3$N@C$_{80}$) system is found.

4 Summary and Outlook

In this chapter, we have shown the endohedral fullerenes as a widely varied and novel new class of conjugated carbon nanostructures. In particular, the use of a combination of high-energy spectroscopies and state-of-the-art atomic multiplet calculations (including, where appropriate, the effects of charge transfer) has been shown to be a very sensitive and direct probe of the valency of the encapsulated species and of the type of interaction they have with the carbon host cage. These interactions span from dominantly ionic, such as in Gd@C$_{82}$, through to systems such as Sc$_2$@C$_{84}$ where a significant degree of Sc–C hybridisation takes place. The metal ions take on valencies ranging from pure trivalent (Gd@C$_{82}$, Ce$_2$@C$_{76}$) through intermediate between tri- and divalent (Sc$_2$@C$_{84}$ and Sc$_3$N@C$_{80}$) to pure divalent (Tm@C$_{82}$), indicating that encapsulation can even go so far as to render unusual, low oxidation states air stable. On the other hand, the encapsulation of the endohedral species and the concurrent charge transfer to the fullerene cage can also lead to a stabilisation of particular higher fullerene isomers which are not stable in the uncharged state, such as the highly symmetric $I_h$ isomer of C$_{80}$ in Sc$_3$N@C$_{80}$.

The trends in endohedral research point towards increased synthesis and investigation of systems containing transition-metal ions, either in the form of elemental or inorganic clusters. As the two Sc endohedrals discussed here have shown, the 3d levels are more likely to participate in hybridisation and thus exhibit a range of interactions between guest and host fullerene than their 4f
cousins from the rare-earth series. Another recognisable trend involves the study of systems in which fullerene molecules, endohedral fullerenes or other materials have been incorporated as the ‘filling’ of carbon nanotubes. Although nanoscopic probes such as electron microscopy are in the forefront of such investigations, high-energy spectroscopy also has a role to play, in particular when exploiting the site-selectivity available when involving core levels in the excitation under consideration.

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5 References

2. In the accepted molecular label given to an endohedral fullerene – such as Y@C82 – the species before the sign @ denotes the ‘content’ of the fullerene molecule, the latter being denoted by Cn.
17. Distillation is a method in which a fulleride film with a nominal starting composition MxCy is heated for a prolonged period in ultrahigh vacuum. Depending on the starting composition and the stable phases of the system, either fullerene molecules or metal intercalant atoms evaporate from the film, driving the composition towards a stable phase [see Poirier DM, Weaver JH (1993) Phys Rev B 47:10959]. This method enables phase-pure films of intercalated fullerenes to be produced for spectroscopic studies. The low quantities in...
which most endohedral fullerenes are available unfortunately precludes the application of this method.

The Jahn–Teller Effect and Fullerene Ferromagnets

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Abstract The discovery of C₆₀ and other members of the fullerene family opened new horizons in the design and synthesis of new molecular-based materials. The discovery that TDAE-C₆₀ exhibits a transition to a ferromagnetic ground state at an unusually high transition temperature Tₐ=16 K has been particularly exciting. Intensive work for more than a decade revealed a unique correlation between spin and orientational ordering of Jahn–Teller-distorted C₆₀ ions. In this chapter, we first review the physics of the Jahn–Teller effect in C₆₀ ions. Then we describe the structural, electronic, and magnetic properties of TDAE-C₆₀. We also show magnetic resonance data, which provide strong evidence for the correlation between orbital and spin ordering in TDAE-C₆₀ and allow for the determination of the Jahn–Teller dynamics.

Keywords Fullerenes · Ferromagnetism · Jahn–Teller effect · Magnetic resonance · Muon spin relaxation · Structural properties · Orbital ordering

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1 Introduction

According to Heisenberg [1] ferromagnetism is not expected to be found in compounds consisting only of first row elements such as carbon, hydrogen, oxygen, and nitrogen. In fact only a few purely organic ferromagnets have been discovered so far and the corresponding transition temperatures \( T_C \) are very low. In view of that, it is rather remarkable that the \( C_{60} \)-based purely organic 1:1 charge-transfer compound TDAE\(^+\)C\(_{60}\) (TDAE=tetrakis-dimethylaminoethylene) exhibits a ferromagnetic transition at \( T_C=16 \) K [2]. The transition temperature is the highest of all known nonpolymeric purely organic ferromagnets.

Magnetic materials, which we are using at present, are inorganic materials based on metallic or ionic lattices. Iron and SmCo\(_5\) are just two of the most typical examples of such metallic magnetic materials. Their magnetic moment is large and nonzero even at room temperature, but as inorganic materials they are heavy, opaque, and hardly dissolvable in water or organic solvents. This sometimes makes the processing of these materials difficult and urges the search for alternative materials.

Organic bulk ferromagnetism was discovered in 1991 [3]. There has been enormous progress in the design and synthesis of molecular-based magnetic...
materials [4] with large molecular units as building blocks during the past few years. One can divide organic molecules which are open-shell entities into two different groups containing either neutral, localized unpaired electron-containing functional groups (free electrons) or charged species (radical ions). The nitroxyls are examples of members of the former category and are very stable and well suited for the study of their solid-state magnetic properties. Radical ions representing the second group result from electron transfer from the $\pi$-orbitals of an electron-rich molecule or from the transfer of an electron to the $\pi$ molecular orbital of an electron-deficient molecule. Whereas classical magnets are atom based, the first molecule-based magnet, Fe(S$_2$CNET$_2$)$_2$Cl, was reported in 1967 with a $T_C=2.46$ K [5]. In organic systems, the magnetic moments are derived exclusively from unpaired electron spins residing in $p$-electron orbitals, whereas all classical magnets possess unpaired electron spins that contribute to magnetic ordering in $d$- or $f$-orbitals. This results in weaker exchange interactions and in a small magnetic anisotropy due to weak spin–orbit coupling if the molecule is composed of the first row elements H, N, C, and O.

In the search for organic magnets one often looks for a suitable electron donor and electron acceptor. Strong organic electron donors have been known for a long time [6, 7]. The list of organic acceptors is also getting longer every day. However, the field really started moving in a new direction in 1991 with the discovery [8] of the buckminsterfullerene molecule C$_60$ (Fig. 1) and other higher C$_{2n}$ molecules [9]. In C$_{60}$, 60 carbon atoms are arranged in the form of a truncated icosahedron (soccer ball). This molecule has the high symmetry of an icosahedron (point group $I_h$) with six five-fold axes, ten three-fold axes, fifteen two-fold symmetry axes, and inversion symmetry. From an organic chemist’s perspective, C$_{60}$ represents an entirely new type of organic molecule and opens new horizons in the design and synthesis of novel compounds. To a physicist, on the other hand, the C$_{60}$ molecule represents a highly symmetric, stable molecular analogue of a very large atom, which can adopt in the solid state a crystal structure with relatively large interstitial sites that can be filled with atomic or even molecular host units.

A$_3$C$_{60}$ compounds (A=Na, K, Rb, Cs) are known to exhibit moderately high $T_C$ superconductivity. Whereas the origin of superconductivity in these systems now seems to be well understood, the nature of the magnetic transition in TDAE-C$_{60}$ discovered in 1991 remained controversial for a rather long time. Conflicting models such as itinerant ferromagnetism, superparamagnetism, spin-glass behavior, and spin-canted weak ferromagnetism have been proposed. Detailed conductivity measurements have ruled out itinerant ferromagnetism. Ferromagnetic resonance in a TDAE-C$_{60}$ single crystal has been observed in the radiofrequency region. The results showed that TDAE-C$_{60}$ behaves as an easy axis three-dimensional Heisenberg ferromagnet with an exceptionally small anisotropy field. The easy axis coincides with the direction of the closest approach of the C$_{60}$ ions. $^{13}$C NMR measurements have shown that the C$_{60}$ ions undergo a Jahn–Teller distortion resulting in a belt-like redistribution of the unpaired electron spin density, with the maximum at the equator and the minimum at the poles. It is this redistribution which seems to be responsible for the relatively high $T_C$ in TDAE-C$_{60}$. X-ray studies have further shown that the long molecular axes
of the neighboring Jahn–Teller-distorted C\textsubscript{60} ions are perpendicular to each other leading to ferromagnetic coupling.

It is the purpose of this chapter to review the recent developments in this field with a particular emphasis on the interplay between orbital ordering of the Jahn–Teller-distorted C\textsubscript{60} ions and spin ordering leading to the ferromagnetic state.

2
Jahn–Teller Effect in Negatively Charged C\textsubscript{60}

2.1 Jahn–Teller Effect in C\textsubscript{60}

There is a large class of compounds containing ions with an orbital electronic degeneracy – the so-called Jahn–Teller (JT) systems. The positively or negatively charged icosahedral C\textsubscript{60} ion – created when additional charges or holes are introduced into the C\textsubscript{60} molecule – is a prominent member of this family. The interplay between orbitals and spins often leads to interesting magnetic structures. For instance, the size and sign of the magnetic interaction between two JT-distorted C\textsubscript{60} ions depends on the relative orientation of the long molecular axes of the two C\textsubscript{60} anions. It has been shown [10] that the magnetic interaction is antiferromagnetic if the two axes are parallel and ferromagnetic if they are perpendicular to each other. Thus, if we are able to control the relative orientation of the two neighboring C\textsubscript{60} molecules then we can control the magnetic properties as well! The key factor here is the Jahn–Teller effect.

The Jahn–Teller effect is associated with electron–lattice interactions. In particular, when the electronic states of the nondistorted molecule are degenerate, the Jahn–Teller effect removes this degeneracy by distorting the molecule. Orbital ordering can also lead to a cooperative Jahn–Teller distortion and three-dimensional ferromagnetic ordering.

The importance of the Jahn–Teller effect was first recognized immediately after the discovery of C\textsubscript{60} in connection with the occurrence of superconductiv-
ity in $A_3C_{60}$ [11, 12]. One may expect that adding electrons to the lowest unoccupied three-fold degenerate $t_{1u}$ molecular orbital (LUMO) should lead to the Jahn–Teller distortion of the molecule. Group theory predicts linear coupling to molecular distortions of $A_g, T_{1g}$ and $H_s$ symmetry. Normal-mode displacements have been calculated by Weeks and Harter [13, 14]. The $T_{1g}$ mode is asymmetric and thus cannot contribute to the linear Jahn–Teller coupling. On the other hand, $A_g$ is fully symmetric and thus cannot lower the symmetry of the molecule. This leaves only quadrupolar $H_s$ vibrations to be coupled to a given electronic state [15, 16]. The Jahn–Teller coupling matrix has been derived in analogy with a silicon vacancy [11, 17].

\[
V_{JT}^p = \frac{I_p}{2} \begin{pmatrix}
-Q_{p\theta} + \sqrt{3}Q_{p\varepsilon} & \sqrt{3}Q_{p\zeta} & \sqrt{3}Q_{p\eta} \\
\sqrt{3}Q_{p\zeta} & -Q_{p\theta} + \sqrt{3}Q_{p\varepsilon} & \sqrt{3}Q_{p\xi} \\
\sqrt{3}Q_{p\eta} & \sqrt{3}Q_{p\xi} & \sqrt{2}Q_{p\theta}
\end{pmatrix}
\]  

(1)

where $I_p$ is the energy per unit displacement of the $p$-th mode, $Q_{p\alpha}$ is the normal coordinate and $\alpha = \theta, \varepsilon, \zeta, \eta, \xi$ is the degeneracy index [11]. The existence of a Jahn–Teller coupling leads to different energy surfaces, which can be calculated by adding $V_{JT}^p$ to the elastic terms. The high icosahedral symmetry of neutral $C_{60}$ is then reduced. Different point groups of lower symmetries for distorted $C_{60}^{n-}$ ions are predicted (Table 1). The Jahn–Teller distortions are generally fairly small in $C_{60}^{n-}$ ions – less than 0.02 Å – leading to orbital splittings of less than 0.1 eV [17]. This is because the $C_{60}$ molecule itself has a very rigid structure and added electrons are distributed all over the $C_{60}$ sphere. An immediate effect of additional electrons on the structure of the $C_{60}^{n-}$ ion is that the short (double) bonds connecting the pentagons slightly increase in length and the average radius of the $C_{60}^{n-}$ increases with $n$ (Table 1; Fig. 2) [18]. We mention here that electronic correlations enhance the coupling of electrons to the modes involving bond alternation, such as the pentagonal pinch mode [19].

Orbital splitting due to the Jahn–Teller effect represents around half of the bandwidth in the solid $A_nC_{60}$ ($A=$Na, K, Rb, Cs). This means that static Jahn–Teller distortions of the $C_{60}^{n-}$ ions will not necessarily survive in metallic fullerenes.

### Table 1 Distortion structural parameters of $C_{60}^{n-}$ (after [18])

<table>
<thead>
<tr>
<th>$C_{60}^{n-}$</th>
<th>Point group</th>
<th>$R$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{60}$</td>
<td>$D_{3d}$</td>
<td>3.5379</td>
</tr>
<tr>
<td>$C_{2-}$</td>
<td>$D_{2h}$</td>
<td>3.5417</td>
</tr>
<tr>
<td>$C_{6-}$</td>
<td>$D_{3d}$</td>
<td>3.5419</td>
</tr>
<tr>
<td>$C_{4-}$</td>
<td>$C_i$</td>
<td>3.5469</td>
</tr>
<tr>
<td>$C_{5-}$</td>
<td>$D_{5d}$</td>
<td>3.5526</td>
</tr>
<tr>
<td>$C_{7-}$</td>
<td>$D_{2h}$</td>
<td>3.5592</td>
</tr>
</tbody>
</table>
2.2 Jahn–Teller Effect in C$_{60}$

In TDAE-C$_{60}$ – exhibiting Heisenberg ferromagnetism – only one electron should be transferred from the donor TDAE molecule to C$_{60}$. We will therefore first review in more detail the Jahn–Teller-distorted C$_{60}$– ion. Three different structures of Jahn–Teller-distorted C$_{60}$– ions were identified having $D_{5d}$, $D_{3d}$, and $D_{2h}$ symmetry (Fig. 3) [10]. They appear almost degenerate and are for about 2 kcal/mol more stable than the nondistorted $I_h$ symmetric structure. There are 15 equivalent structures in the $D_{2h}$ ion. Similarly there are ten equivalent $D_{3d}$ and six equivalent $D_{5d}$ structures. This makes altogether 31 possible structures with nearly equal energy. The C$_{60}$ ion is thus, at least at high temperatures, expected to tunnel or jump between these potential minima with some temperature-dependent frequency leading to pseudorotations of the distorted ion. If the tunneling or classical hopping occurs on the time scale of molecular vibrations, then no static distortion will be observed by most of the experiments.

The most interesting feature about the Jahn–Teller-distorted C$_{60}$– ion is the electron density of the singly occupied molecular orbital (SOMO). It turns out that the SOMO is localized mainly around the equator and has only very small electron density around the poles, through which the principal symmetry axis
passes. As a result the CC bonds change very little on the poles. Much more drastic changes are predicted for CC bonds on the equator with C=C bonds getting slightly longer and C–C bonds slightly shorter. After accepting one electron the C$_{60}$ molecule thus becomes ellipsoidal with the C$_{60}^-$ ion being slightly stretched along the principal symmetry axis. The axis of elongation dictates the orientation of the SOMO and the resulting charge and spin densities in various deformed structures. It is shown that the spin densities are concentrated in the vicinity of the equator (Fig. 4). The spin densities on a particular carbon atom in the C$_{60}^-$ cage may vary quite substantially, i.e., from 0 to 0.059 of an electron spin [18], or in other words even up to 3.5 times the magnitude expected for the nondistorted icosahedral molecule. This should lead to large hyperfine electron–$^{13}$C nuclear couplings, which should be detectable by $^{13}$C NMR.

Finally we would like to mention that the Jahn–Teller distortion of the C$_{60}^-$ ion is sometimes labeled as a polaron effect in analogy with conducting polymers [21, 22]. Freedman [21] and Harigaya [22] both used the Su–Schrieffer–Heeger (SSH) model [23] to investigate the C$_{60}^-$ ion. Neglecting the intermolecular hopping and without any symmetry restriction they obtained a distortion of the C$_{60}^-$ ion. The structural deformation of the C$_{60}^-$ ion occurs around the equator perpendicular to the fivefold axis. The dimerization is suppressed along the equator as already predicted by the formal Jahn–Teller analysis. It has also been found [22] that the additional charges accumulate along the equatorial line of the molecule pointing to a very nonuniform charge and spin distribution on the molecule.

![Fig. 3](https://example.com/fig3)  
Unrestricted Hartree–Fock (UHF) optimized structures (in Å) of C$_{60}^-$ ion of $D_{5d}$, $D_{3d}$, and $D_{2h}$ symmetry. The bond distances are shown only for the fragment of hatched carbon atoms. *Italics* are center–carbon distances. *Atom numbering* denotes symmetry-unique carbons (reproduced from [20])
2.3 Experimental Evidence for the Jahn–Teller Effect in Charged C_{60}^{n–} Ions

Ever since the discovery of moderately high-temperature superconductivity in A_{3}C_{60} solids (A=Li, Na, K, Rb, Cs), considerable activity has been devoted to the investigation of the doping-induced changes in the vibrational modes of C_{60}^{n–} ions. The work was focused on the question whether the superconducting pairing is mediated by the vibrational modes and if so, by which modes. Using inelastic neutron scattering librational modes of C_{60}, samples were studied by several groups [24–26] and then compared with the analogous modes of C_{60}^{n–} in alkali metal-doped C_{60} [27]. Well-defined peaks were observed at room temperature at 3.59 and 5.49 meV in K_{3}C_{60} and Rb_{6}C_{60}, respectively. The dependence of their intensities on the scattering vector shows that they are due to the small-amplitude librations. No anomalous behavior of the librational peak has been observed on cooling through the superconducting transition suggesting that the electron–librational coupling is very weak [27].

Optical spectroscopy should provide fewer but less ambiguous results. The active Raman and IR C_{60}^{n–} molecular modes are – although shifted due to the charge transfer – largely independent of the dopand atom, mass, or crystal structure [28, 29]. This result suggests that the principal role of dopands is to contribute electrons to the C_{60} molecular orbital. In Raman studies of doped C_{60}^{n–} both A_{g} and H_{g} modes were observed [28–34]. In K_{3}C_{60} and Rb_{3}C_{60} strongly broadened H_{g}–derived modes were observed with a typically Breit–Wigner–Fano lineshape [28, 34]. Although the broadening of the H_{g}–derived modes in K_{3}C_{60} could be a result of the Jahn–Teller distortion due to the splitting of these modes, when the molecular symmetry is lowered, it has been rather associated with the enhanced coupling between the phonons and low-energy electronic excitations.

Near-IR investigations of frozen C_{60} solutions on the other hand were cited as experimental evidence for the Jahn–Teller effect [35–39]. The fact that the electronic absorption of C_{60} has a rich vibrational structure suggests that the symmetry of the C_{60}^{n–} ion is lower than I_{6}. Interestingly it has been found [36]...
that the $C_{60}^-$ ion in nonpolar media (such as rare gas matrices) prefers $D_{5d}$ or $D_{3d}$ Jahn–Teller configurations, while in polar media such as 2-methyltetrahydrofuran (MTHF) it goes to a $D_{2h}$ Jahn–Teller configuration.

When a Jahn–Teller-distorted $C_{60}^-$ molecule is placed in a solid-state environment, strain or crystal-field perturbations may play a decisive role in the selection and/or enhancement of the Jahn–Teller-distorted configuration. In an attempt to investigate the Jahn–Teller-distorted $C_{60}^-$ molecules in the solid state, $C_{60}$-tetraphenylphosphonium iodide has been synthesized and studied [40]. The well-known $F_{1u}(1)$ and $F_{1u}(2)$ modes were found to split into doublets at room temperature indicating a $D_{5d}$ or $D_{3d}$ and not a $D_{2h}$ Jahn–Teller configuration. These results are consistent with a dynamic Jahn–Teller effect in the strong coupling limit or with a static distortion stabilized by the low-symmetry perturbations.

Electron paramagnetic resonance (EPR) has provided a great deal of evidence for a Jahn–Teller effect in charged $C_{60}^-$ ions and photoexcited $C_{60}^-$. Neutral $C_{60}$ molecules have no unpaired spins and therefore do not exhibit an EPR signal in the ground state. It is, however, possible to observe the EPR signal from the optically excited triplet state where $C_{60}$ is expected to undergo a Jahn–Teller distortion [41]. The triplet EPR spectra of photoexcited $C_{60}$ show a characteristic lineshape broadening (Fig. 5), which suggests random exchange between different Jahn–Teller configurations at very low temperatures [42, 43]. Observations of zero-field splitting in the excited triplet state demonstrate that the molecule undergoes a distortion to a lower symmetry. Bennati et al. [43] simulated the photoexcited triplet EPR signal of $C_{60}$ in frozen toluene, assuming exchange of Jahn–Teller-distorted $^3C_{60}$ between all equivalent sites allowed for the $D_{3d}$ symmetry of the molecule. The exchange rate is weakly temperature dependent.
and strongly suggests that the dynamic process is due to tunneling between Jahn–Teller-distorted states.

Contrary to undoped \( \text{C}_{60} \), unpaired electrons exist in doped \( \text{C}_{60}^{-} \) and thus the EPR signal can be measured \([38, 39, 44]\) in the ground state. The temperature dependence of the EPR signal of the \( \text{C}_{60}^{-} \) ion dissolved in CH\(_2\)Cl\(_2\) as prepared by electrolysis has been measured \([39]\). At room temperature the \( g \)-factor value is 1.9982. The observed shift is \( \Delta g = -0.0041 \) relative to the free electron value \( g_e = 2.0023 \). The energy gap between the singly occupied energy level and the other two energy levels that had, before the distortion, belonged to the triply degenerate \( t_{1u} \) orbital is about 70 cm\(^{-1}\). The EPR line is very narrow with a typical peak-to-peak linewidth of a few Gauss. On cooling the EPR line becomes anisotropic, which can be attributed to a Jahn–Teller distortion of the molecule. We mention here that the electrochemically prepared anions \( \text{C}_{60}^{2-} \) and \( \text{C}_{60}^{3-} \) were also detected by EPR and many studies can be found in the literature \([45–47]\).

EPR was the key experimental tool to suggest the occurrence of the Jahn–Teller effect in \( \text{C}_{60} \) in the solid state. Gotschy et al. \([48]\) measured the CW X-band EPR signal in \((\text{P(C}_6\text{H}_5)_4)_2\text{C}_{60}\text{I}\), which is a paramagnetic salt. Above 140 K, the EPR line is homogeneous and very broad – the peak-to-peak linewidth is around 40 G at room temperature. However below 140 K, the line splits into two lines (Fig. 6) and the splitting increases with decreasing temperature. The data have been interpreted in terms of a dynamic Jahn–Teller effect. In this crystal the Jahn–Teller deformation becomes static on the EPR time scale below 70 K.

Völkel et al \([49]\) used pulsed EPR to find experimental evidence for the Jahn–Teller effect in \( \text{C}_{60} \)-tetraphenylphosphorium chloride \((\text{Ph}_4\text{P}^+\text{C}_{60}^-) \cdot 2(\text{Ph}_4\text{P}^+\text{Cl}_x)\) salt \([50, 51]\). They combined the measurements of the EPR linewidth with the measurements of the transversal and longitudinal relaxation times \( T_2 \) and \( T_1 \) between 4 K and room temperature (Fig. 7). The relaxation at low temperatures, i.e., below 40 K, is governed by three competing mechanisms: exchange narrowing due to Heisenberg exchange interaction, magnetic fluctuations with typical correlation times comparable to the EPR time scale, and a slow

![Fig. 6](image_url)  
**Fig. 6** Splitting of the EPR line in \((\text{P(C}_6\text{H}_5)_4)_2\text{C}_{60}\text{I}\) as a function of temperature. The splitting has been attributed to the Jahn–Teller effect, which is static below 70 K and dynamic above that temperature. (Reproduced from \([48]\))
reorientation of the $\text{C}_{60}$ anion. However above 40 K the electronic spin–lattice relaxation time rapidly increases with increasing temperature. The temperature dependence of the electronic spin–lattice relaxation time ($T_{1e}$) has been fitted to a simple exponential form

$$T_{1e}^{-1} \propto \exp\left(-\frac{\Delta}{kT}\right)$$

where the characteristic energy $\Delta/k=219$ K corresponds to $152$ cm$^{-1}$ [49]. This energy is very close to the estimated energy gain due to the Jahn–Teller distortion. This means that a low-lying excited state exists which makes the Orbach relaxation process [52, 53] possible.

2.4 Jahn–Teller Effect in Alkali-Doped $\text{C}_{60}$

Brouet et al. [54–56] suggested that the Jahn–Teller effect could be responsible for the formation of spin-singlets in the low-temperature cubic phase of CsC$_{60}$ [57]. $^{137}$Cs NMR clearly showed three distinct lines, all of them being intrinsic and mixed on the microscopic scale as evidenced from the SEDOR experiments. These three $^{137}$Cs NMR lines correspond to the cases where $\text{C}_{60}$ molecules are charged with two, one, or no electrons. The stabilization of $\text{C}_{60}^2$ in the simple cubic phase of CsC$_{60}$ is particularly intriguing as it is believed that it is the result of a delicate balance between intraball Coulomb repulsion and the Jahn–Teller effect.

The fact that Brouet et al. [56] observed a separate $^{137}$Cs NMR line corresponding to the spin-singlet state of $\text{C}_{60}^2$ means that the lifetime of this excitation is rather long. It must certainly be longer than the characteristic time scale of the NMR experiment. This means that these excitations are static rather than dynamic.
It is interesting to note that the same group also found evidence for the formation of Jahn–Teller-stabilized spin-singlets (C_{60}^{2–} and C_{60}^{4–}) also in Na_{2}C_{60} and Na_{2}CsC_{60} [55]. This system is at low temperatures orientationally ordered and crystallizes in the Pa3 space group. This suggests that orientational order/disorder of C_{60}^{n–} ions may be important for the occurrence of a static Jahn–Teller effect in these compounds.

2.5 Jahn–Teller Effect in C_{60} and Magnetic Interactions

If there were no distortion, the \( t_{1u} \) energy levels of C_{60} would be threefold degenerate. Dopands, like alkali metals or TDAE, donate one electron to this orbital. If the electrons are highly delocalized, so that they can be viewed as itinerant electrons, two intermediate species C_{60}^{2–} and C_{60} are formed. Within the framework of the McConnell mechanism [58] the admixture of the high-energy charge-transfer states (Fig. 8a, right) with the degenerate ground state lowers the total energy and stabilizes antiferromagnetic coupling. If, however, the ground state is degenerate, ferromagnetic coupling is favored (Fig. 8b). This led Wudl et al. to propose that a ferromagnetic organic metal modification of the McConnell mechanism may be applied to TDAE-C_{60} [59].

However there are serious problems with this proposal. First, TDAE-C_{60} is not a metal. Second, the Jahn–Teller effect lifts the degeneracy of the originally threefold degenerate \( t_{1u} \) molecular orbital. For instance the Jahn–Teller distortion of the C_{60} molecule leading to the \( D_{2h} \) structure will result in three states. One of them, assigned as LUMO_{z}, corresponds to the belt-like charge density distribution around the C_{60} elongated z-axis and has in an orthorhombic environment a lower energy than the other two, assigned as LUMO_{x} and LUMO_{y} [60]. Since the transfer integral for the exchange of an electron between two orthogonal orbitals on adjacent molecules is zero, the magnetic coupling strongly depends on the relative orientation of the two neighboring C_{60} molecules. As pointed out by Kawamoto [60], the ground state should be antiferromagnetic (Fig. 9a) if the long axes of two C_{60} ions are parallel to each other. If, however, the axes of the Jahn–Teller elongation of the two neighboring C_{60} ions are orthogonal to each other, the coupling

![Fig. 8a, b](image-url)  
**Fig. 8a, b** Schematic illustration of the McConnell mechanism leading to a antiferromagnetic and b ferromagnetic coupling
should be ferromagnetic (Fig. 9b). If this is so, the TDAE-C$_{60}$ crystal should be viewed as an assembly of C$_{60}$– chains where, within the individual chain, the axes of the Jahn–Teller distortion of the two adjacent C$_{60}$– molecules reorient by 90° [60].

This suggestion has been further supported by theoretical investigations of the angular dependence of the exchange interaction between two C$_{60}$ ions [61]. It was found that the exchange interaction is considerably anisotropic and that the magnetic interaction depends not so much on the distance between the two neighboring C$_{60}$ ions as on the orientation of each C$_{60}$. Interestingly, the exchange interaction can change from antiferromagnetic to ferromagnetic if one rotates the C$_{60}$ ion [61].

An example of a Jahn–Teller-distorted crystal structure with possible three-dimensional ferromagnetic ordering is shown in Fig. 10. Here the elongated axes of the Jahn–Teller-distorted C$_{60}$ are perpendicular to each other not only for intrachain nearest neighbors but also for interchain nearest neighbors.

Fig. 9a, b If the axes of the Jahn–Teller distortion of the two adjacent C$_{60}$ ions coincide, then the coupling is antiferromagnetic (a). If they are orthogonal, the coupling should be ferromagnetic (b)

Fig. 10 A possible Jahn–Teller-distorted C$_{60}$ arrangement in the TDAE-C$_{60}$ crystal leading to ferromagnetic phenomena. Ellipsoids represent Jahn–Teller-distorted C$_{60}$ ions (reproduced from [10])
3 Review of the Magnetic Properties of TDAE-C₆₀

3.1 Introduction

The purpose of this section is to review the magnetic properties of the ferromagnetic fulleride tetrakis-dimethylaminoethylene-C₆₀ (TDAE-C₆₀) (Fig. 11), discovered by F. Wudl and coworkers at the University of California, Santa Barbara [2]. At the time of discovery, the Curie temperature, $T_C=16$ K, of TDAE-C₆₀ was one order of magnitude higher than the existing highest transition temperature for an organic ferromagnet [62], and brought the field of $p$-electron ferromagnetism research into the mainstream.

When the group of Professor Wudl measured the magnetic properties of powdered TDAE-C₆₀ [2], a steep rise in the real part of the ac susceptibility was evident below 16 K, implying the occurrence of a ferromagnetic-type transition at a surprisingly high transition temperature, $T_C=16$ K, for a compound comprising only elements of the first row (C, N, H) of the periodic table. After TDAE-C₆₀ was discovered, numerous experiments were performed on both powders and single crystalline samples, leading to a comprehensive understanding of its intriguing behavior [63–65]. However, very few new compounds have been found to show similar ferromagnetic behavior, and until very recently [66] TDAE-C₆₀ remained the C₆₀–based compound with the highest $T_C$. For example, TDAE-C₇₀ [67–69] and other TDAE-doped higher fullerene derivatives [70] show no evidence for a ferromagnetic state down to 4 K. This is also true when TDAE is substituted with other organic electron donors [71, 72]. Although there have been some reports of possible ferromagnetism at higher temperatures, until now such vaguely defined ferromagnetic C₆₀ phases have failed the reproducibility test [73].

Soon after the discovery of ferromagnetism in TDAE-C₆₀, it was realized that the ferromagnetic transition in TDAE-C₆₀ is not a conventional type of transition, which could be simply treated within some standard textbook theory. Some of the puzzling properties of TDAE-C₆₀ were described in detail in the original report on its synthesis and magnetic characterization [2]: (i) despite the sharp increase of the magnetization below $T_C$, its temperature dependence did not follow conventional mean field theory behavior; (ii) within experimental error, no hysteresis was observed between measurements under cooling and heating.

Fig. 11 The TDAE molecule donates one of its electrons to the C₆₀ molecule producing the TDAE⁺–C₆₀ charge-transfer compound
protocols; (iii) similarly, the coercive field and the remanent magnetization were found to be zero; and (iv) the spontaneous magnetization was very small, leading to a low-temperature saturation moment of \(\sim 0.11 \mu_B/C_{60}\). No EPR line corresponding to the hole at the TDAE\(^+\) ion has been observed in addition to the C\(_{60}\) EPR line. In order to explain these – at first sight contradictory – magnetic properties, different proposals for the ground state appeared in the early literature, describing TDAE-C\(_{60}\) as an itinerant ferromagnet [2], a superparamagnet [74], a spin-glass [75], or a weak ferromagnet [76].

In the next few subsections we will describe in detail the lattice and electronic structure, and describe the results of the most important experiments, which determine the bulk magnetic properties of TDAE-C\(_{60}\).

### 3.2 Modifications of TDAE-C\(_{60}\)

It is well known that TDAE-C\(_{60}\) exists in at least two different modifications [77, 78] (\(\alpha\) and \(\alpha'\)). Single crystals of the modification \(\alpha\), exhibiting a ferromagnetic transition at 16 K, are grown from the toluene solution at or above room temperature. If, however, the crystals are grown around 0 °C another modification (here designated as modification \(\alpha'\)) is obtained which is also paramagnetic at room temperature but does not show the ferromagnetic transition at low temperatures. If \(\alpha'\) crystals are kept for a prolonged time at or above room temperature, they gradually transform to the modification \(\alpha\) exhibiting the ferromagnetic transition. The transition from \(\alpha'\) to \(\alpha\) modification happens much faster in powder TDAE-C\(_{60}\) samples. This suggests that the presence of local strains may lead to a crystal structures having different magnetic properties.

The difference between these two modifications is rather subtle. For instance, at room temperature the ESR signal is nearly the same in both modifications and the ESR \(g\)-factor values of both modifications nearly coincide. The difference between the two modifications can be observed only on cooling (Fig. 12). Until 170 K the ESR linewidth and shape of the ESR spectra of the two modifications are practically identical. Between room temperature and 170 K – where the C\(_{60}\) rotation freezes out – the width is nearly temperature independent and amounts to around 20 G. Below 170 K the width decreases to about 2 G as a result of exchange narrowing due to the increase of the overlap of the electronic wave function on the neighboring C\(_{60}\) ions. Below 20 K the intensity and the linewidth of the ESR line of the modification \(\alpha\), undergoing the ferromagnetic transition, strongly increases with decreasing temperature. The ESR linewidth of the modification \(\alpha'\), which does not show the ferromagnetic transition, is nearly temperature independent down to the lowest temperature studied, whereas the ESR signal intensity strongly decreases [79]. The position of the X-band EPR resonance signal of the ferromagnetic modification \(\alpha\) shifts at \(T_c=16\) K for about 60 G. No such shift is seen in the position of the EPR signal of nonferromagnetic modification \(\alpha'\). One can thus conclude that no long-range magnetic ordering occurs in the \(\alpha'\) modification. In fact some ESR and \(^1\text{H}\) NMR measurements on the \(\alpha'\) modification also showed evidence for a spin gap in the magnetic excitation spectra [79]. Although it is not quite clear at the moment what this spin gap
really represents one can speculate that it is due to the spin pairing. This can explain consistently the reduction of the effective number of spins per formula unit in the α′ modification [80] as well as the temperature dependence of the ESR susceptibility [78, 79] and of the ¹H spin–lattice relaxation [79]. It is also reminiscent to the formation of Jahn–Teller stabilized spin singlets in some alkali-doped C₆₀ compounds [54–56].

Finally we would like to mention that application of high pressures may even lead to a polymeric phase [81]. Increasing the hydrostatic pressure up to 9 kbar on a TDAE-C₆₀ single crystal gradually decreases $T_C$. The transition temperature approximately follows a relation $T_C(p)=T_C(0)(1–ap^2)$ where $a$ is a constant and $p$ is the hydrostatic pressure. At around $p=9$ kbar $T_C$ is 0 K (or close to 0). For such high pressures the ESR linewidth remains narrow even after releasing the pressure. In a pressure-released sample x-ray diffraction data at 89 K yielded evidence for the formation of C₆₀ polymeric chains along the crystal $c$-axis [81]. The C₆₀–C₆₀ distance is reduced to 9.17 Å, a value comparable to the C₆₀–C₆₀ distance found in the orthorhombic polymeric phase of RbC₆₀ [82]. The magnetic properties of the polymeric phase of TDAE-C₆₀ – as studied by ESR [81] – are interesting as well. Suddenly a new ESR signal can be observed. Its ESR $g$-factor

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**Fig. 12a, b** A comparison of the temperature dependence of the X-band ESR linewidth in a nonferromagnetic α′ modification and b ferromagnetic α modification.
value 2.0028 is close to the one expected for the TDAE$^+$ $g$-factor value (2.0036). The ground state of the polymeric phase is paramagnetic with a very small Curie–Weiss temperature $\theta=-4$ K.

### 3.3 Crystal Structure of the Ferromagnetic $\alpha$ Modification

The TDAE-C$_{60}$ crystal structure was for a long time a matter of some controversy. The confusion most probably came from the fact that the early samples studied were never really single phase, but were rather mixtures of different modifications. In this subsection we will focus on the crystal structure of the ferromagnetic $\alpha$ modification and the properties of other modifications will be just briefly commented on.

When TDAE (a liquid at room temperature) is added to C$_{60}$ in solution, the resulting salt crystallizes as small particles, which can be removed by filtration. TDAE$^+$C$_{60}$ is a charge-transfer salt with a monoclinic structure, different from the high-symmetry cubic structures of pristine C$_{60}$ and its alkali metal-intercalated derivatives [83].

Stephens et al. determined the lattice structure of powdered TDAE-C$_{60}$ to be monoclinic $C2/m$ with one formula unit per unit cell [84]. However, a structural analysis performed on single crystals [85] showed the room temperature structure to be monoclinic with unit cell dimensions $a=15.858(2)$ Å, $b=12.998(2)$ Å, $c=19.987(2)$ Å, $\beta=93.37^\circ$ and four formula units per unit cell. The correct space group was found to be $C2/c$ and not $C2/m$ as originally reported from the powder data. The unit cell in fact consists of two subcells, which are stacked along the $c$-direction so that the unit cell size in the $c$-direction is doubled (Fig. 13). In one of the subcells the TDAE ion is shifted by about 0.02 Å along

![Fig. 13](image-url) Schematic room-temperature structure of TDAE-C$_{60}$. Please note that the molecular sizes of C$_{60}$ and TDAE have been reduced in order to make the picture more transparent
the $b$-axis while in the other, the corresponding TDAE ion is shifted by the same distance in the opposite direction. The TDAE coordinates are therefore (0.5, 0.502, 0.75), (0.5, 0.498, 0.25), (0, 0.002, 0.75), and (0, –0.002, 0.25) with the $C=C$ bond parallel to the $c$-axis, whereas the $C_{60}$ coordinates are (0, 0.5, 0), (0, 0.5, 0.5), 0.5, 0, 0), and (0.5, 0, 0.5). The atomic coordinates are collected in Table 2, together with the isotropic displacement parameters. The $C_{60}$–$C_{60}$ center-to-center distance is shortest along the $c$-axis and amounts to 9.99 Å at room temperature. It should be stressed that this distance is shorter than in the cubic $C_{60}$
structure or in the alkali metal-doped $A_3C_{60}$ compounds. In pure undoped $C_{60}$, for instance, the center-to-center distance between two neighboring $C_{60}$ molecules is 10.24 Å. On the other hand, the distance between neighboring $C_{60}$ ions in the $a$–$b$ plane of the TDAE-$C_{60}$ structure is 10.25 Å, i.e., nearly the same as in other cubic $C_{60}$ systems. The difference between the $C_{60}$–$C_{60}$ distance along the crystal $c$-axis and in the $a$–$b$ plane suggests rather anisotropic electronic properties and could have an important impact on the magnetic properties as well.

The $C_{60}$ molecules were found to be executing large amplitude reorientations at room temperature, so that large anisotropic thermal displacement factors of the $C_{60}$ carbon atoms were found. The thermal displacement parameters for some of the $C_{60}$ carbon atoms at room temperature are, in fact, so large that the $C_{60}$ atomic coordinates may well represent only an average over one or more disordered structures involving fractional atomic occupancy. On the other hand, the TDAE N and C atomic coordinates are well-defined already at room temperature.

The low-temperature structure of $\alpha$ TDAE-$C_{60}$ has been solved only recently by Narymbetov et al. [86]. The crystal transforms from a high-temperature, $C$-centered, monoclinic structure to a primitive one at low temperatures. The most interesting characteristic of this low-temperature structure is the way that the neighboring $C_{60}$ ions face each other. It has been proposed that, like in pure $C_{60}$, there exists a “standard” relative orientation [87, 88] of two neighboring $C_{60}$ ions in which electron-rich double bonds face the electron-poor pentagon/hexagon of the neighboring $C_{60}$ molecule. The $C_{60}$ ions thus have different possible packings, which eventually lead to a variation of the magnetic exchange interaction [89] and can explain the fact that TDAE-$C_{60}$ is found in two different magnetic modifications, i.e., the nonferromagnetic $\alpha'$ phase and ferromagnetic $\alpha$ phase.

Another manifestation of the importance of the orientational order/disorder in TDAE-$C_{60}$ has been shown in a recent study by Kambe et al. [90]. The effects of annealing on the magnetic and structural properties were studied in detail. It was found that well-annealed samples undergo a structural phase transition at around 180 K – most probably associated with the $C_{60}$ orientational ordering previously suggested by $^{13}$C NMR [91] and described in the next section – and that in this case the saturation magnetization increases to 0.9(1) $\mu_B/C_{60}$ ion. On the other hand, the as-grown crystals undergo no structural phase transition at least down to 30 K and do not order ferromagnetically. We note, however, that the connection between orientational order and magnetic properties was already studied previously by comparing the magnetic and structural transition in powdered TDAE-$C_{60}$ samples that were slowly cooled in a 9-T magnet and quenched from room temperature to low temperatures in zero magnetic field [92].

### 3.4 Electronic Properties

Since a charge transfer from TDAE to $C_{60}$ leads to a partially filled molecular $t_{1u}$ orbital (Fig. 2), and because of the close contacts of the $C_{60}$ units, it might be expected that TDAE-$C_{60}$ is a metal with a highly anisotropic electronic structure, displaying itinerant ferromagnetism [2]. However, powder infrared absorption
spectroscopy revealed that TDAE-C\textsubscript{60} displayed no Drude tail and exhibited no absorption at low frequencies \cite{93}, implying that the material is most probably an insulator. Microwave absorption measurements \cite{94} supported the insulating character of TDAE-C\textsubscript{60}. The issue was finally settled unambiguously by dc and ac conductivity measurements on single crystals of TDAE-C\textsubscript{60} as a function of temperature. These experiments definitely ruled out the existence of a metallic state and the possibility of an itinerant ferromagnetic ground state below \( T_c = 16 \text{ K} \).

While the fact that TDAE-C\textsubscript{60} is not metallic seems to be now generally accepted, the origin of the insulating state is still open. Arovas et al. suggested that TDAE-C\textsubscript{60} is a Mott insulator \cite{96}. Interestingly they have shown that orbital degeneracy can be represented as an additional “isospin” degree of freedom. In the limit of a one-dimensional model justified by the short interfullerene distance along the crystal \( c \)-axis, several different ground states can be stabilized depending on the crystal fields: (i) an SU(4) antiferromagnet, (ii) a spin-ferromagnet/isospin-antiferromagnet, and (iii) an isospin-ferromagnet/spin-antiferromagnet. This analysis suggested the connection between the orbital and magnetic ordering, i.e., TDAE-C\textsubscript{60} should possess ferromagnetically ordered spins and antiferromagnetically ordered isospins with two different transition temperatures. Taking into account interchain interactions (\( J_\parallel \) they \cite{96} find in the mean field approximation a ferromagnetic transition at \( T_c = \sqrt{J_\parallel J_\perp} \) and an antiferromagnetic isospin transition at \( T_N = J_\perp \). Here \( J_\parallel \) is the intrachain coupling.

Quite different from that, Omerzu et al. proposed that TDAE-C\textsubscript{60} is an Anderson-type insulator where the disorder is due to the orientational disorder of C\textsubscript{60} molecules \cite{95}. This has been concluded from the thermally activated type of the conductivity, which in the temperature range between 100 and 300 K follows an Arrhenius law

\[
\sigma_{dc} = \sigma_0 \exp \left(-\frac{E_a}{kT}\right)
\]

with \( E_{a1} = 0.3 \text{ eV} \) and \( E_{a2} = 0.14 \text{ eV} \) for \( T > 150 \text{ K} \) and \( T < 150 \text{ K} \), respectively. As there is no evidence of an energy gap of the order of 0.2 eV, which would be expected for a semiconductor with a Hubbard gap in the excitonic spectrum due to the antiferromagnetic correlations, the authors concluded that TDAE-C\textsubscript{60} cannot be a Mott insulator. Alternatively they proposed a thermally activated phonon-assisted conductivity \cite{97} \( \sigma \propto \omega \exp\left(-\frac{E_b}{kT}\right) \), where \( E_b \) is the polaron binding energy and \( \omega \) is the rate of rotation of the C\textsubscript{60} ion. It should be stressed however that a randomly frozen out Jahn–Teller distortion can also lead to electron localization and describe the thermally activated conductivity.

3.5 Bulk Magnetic Properties

The temperature dependence of the ac susceptibility in powdered TDAE-C\textsubscript{60} is shown in Fig. 14. A transition to a ferromagnetically ordered state is clearly visible at \( T_C = 16.1 \text{ K} \). The anomaly at 10 K seen in the real part of the susceptibility is related to the broad bump in the imaginary part of the susceptibility.

As already mentioned, the first magnetization studies showed that TDAE-C\textsubscript{60} has no magnetic hysteresis \cite{2} on cooling and heating through \( T_c \) and that the
remanent magnetization is vanishingly small. However, subsequent studies showed that a hysteresis exists and that there is a small, but nonzero, remanent magnetization [98, 99] which is of the order of $10^{-4}$ emuK/g.

A typical ac susceptibility measurement on a TDAE-C$_{60}$ single crystal is shown in Fig. 15. The observed behavior is analogous to that measured in powdered samples except that the magnetic transition in single crystals is much sharper and the anomaly at around 10 K is less pronounced (although not washed away.

**Fig. 14** The real and the imaginary part of the ac susceptibility as a function of temperature for powdered TDAE-C$_{60}$

**Fig. 15** The real and the imaginary part of the ac susceptibility as a function of temperature for TDAE-C$_{60}$ single crystal
The difference between powders and single crystals is most probably due to the larger surface-to-volume ratio in powders (the surface represents a defect) and better crystallinity and/or homogeneity of single crystals. Omerzu et al. studied the critical behavior of the spontaneous magnetization of TDAE-C$_{60}$ single crystals in detail [100]. They managed to determine, for the first time in an organic system, critical exponents associated with the ferromagnetic transition of TDAE-C$_{60}$. The results gave self-consistent values of the critical exponents, in agreement with the behavior expected for a ferromagnetic transition in a system with a certain degree of disorder.

Kambe et al. [101] studied the effects of annealing on the magnetic and structural properties of single crystal TDAE-C$_{60}$. The magnetization of the sample strongly depends on the thermal history of the sample. For instance, in a well-annealed crystal, ferromagnetic ordering was confirmed to be at 16 K and the saturated magnetization corresponded to 0.9±0.1 $\mu_B$ per C$_{60}$ molecule, i.e. to one electronic spin per each C$_{60}$ molecule in agreement with ESR measurements. On the other hand, the as-grown crystal shows no magnetic phase transition and the saturated magnetization is rather small (Fig. 16). In a powder sample the saturated magnetization corresponds to only 0.3 $\mu_B$ per C$_{60}$ molecule [102], most probably as a result of orientational disorder. Subsequent structural studies also revealed a structural phase transition around 180 K in a well-annealed sample [101]. This structural phase transition is absent in as-grown nonferromagnetic single crystals.

**Fig. 16** Magnetization versus magnetic field in a TDAE-C$_{60}$ single crystal. Different measurements correspond to different annealing treatments [101]. Solid circles represent measurements on a well-annealed sample while open circles are measurements on an as-grown crystal. The inset shows the temperature dependence of the magnetization of the well-annealed TDAE-C$_{60}$ single crystal.
Measurements of the time decay of the remanent magnetization in powdered TDAE-C₆₀ by SQUID showed below \( T_C \) the presence of a long tail, which could be described by a stretched exponential function \[103\]. Similar results were also obtained by ESR time decay measurements \[104\].

4 Magnetic Resonance Studies

4.1 Electron Spin Resonance

Different magnetic resonance techniques were used from the very beginning to study the magnetic properties of TDAE-C₆₀. Among them electron spin resonance (ESR) was most widely used. The X-band ESR signal of TDAE-C₆₀ (in powder or single crystalline form) shows a single very strong resonance around \( g \approx 2 \), both above and below \( T_C \). The \( g \)-factor is characteristic of the C₆₀ ion. This is rather surprising for a ferromagnetic system where large internal fields are present. Still another point to be mentioned is that, on the basis of the chemical formula TDAE⁺-C₆₀, one expects two ESR lines: one corresponding to the C₆₀⁻ ion and another corresponding to the TDAE⁺ cation which also contains an unpaired electron. One possible explanation of the presence of only one line would be that TDAE exhibits charge disproportionation, so that instead of TDAE⁺ we would in fact have TDAE²⁺ and TDAE⁰ without any unpaired spins. Plotting the frequencies of the C–N stretching modes 1332 cm⁻¹, 1490 cm⁻¹, and 1625 cm⁻¹ of TDAE⁰, TDAE⁺, and TDAE²⁺ versus the charge state of the TDAE molecule, one can see that the charge state of TDAE-C₆₀ – which exhibits a C–N stretching frequency 1518 cm⁻¹ – is indeed TDAE⁺. The absence of the TDAE⁺ ESR signal thus seems to be due to spin pairing of two neighboring TDAE⁺ units leading to a singlet TDAE state, which is ESR silent. It should also be mentioned that Raman spectra have clearly shown that the charge state of the C₆₀⁻ ion in TDAE-C₆₀ is indeed C₆₀⁻.

The \( g \)-factors for the ESR spectra (Fig. 17) of TDAE-C₆₀ single crystals are \( g_a=2.0001 \), \( g_b=1.999 \), and \( g_c=2.0003 \) at room temperature \[85\]. The linewidths are 20.8, 23.1, and 19.7 G for \( a||H_0 \), \( b||H_0 \), and \( c||H_0 \), respectively. On cooling, a linewidth transition occurs below 150 K (Fig. 12). As will be shown later, ¹³C NMR measurements show that this transition is connected with rotations of the C₆₀ ions. At 50 K the ESR linewidths do not exceed 2 G for all three orientations. Below 45 K a line splitting occurs when \( \vec{H}_0 \) is not parallel to the \( \vec{a} \)-axis. A strongly anisotropic “ferromagnetic”-like line appears in addition to the nearly isotropic “paramagnetic” line, which reflects the presence of the nonmagnetic \( \alpha' \) modification. At 25 K we have two well-separated X-band ESR lines for \( \vec{c}||\vec{H}_0 \) and \( \vec{b}||\vec{H}_0 \) and only one line for \( \vec{a}||\vec{H}_0 \). Below \( T_C=16 \) K the intensities of the “paramagnetic-like” ESR line becomes negligible as compared to the “ferromagnetic-like” ESR line. This line becomes strongly inhomogeneously broadened.

The intensity of the ESR signal is directly proportional to the electronic static susceptibility. The ESR intensity (Fig. 18) at high temperatures in the paramagnetic phase follows approximately the Curie–Weiss law. Interestingly, it has
Fig. 17 The temperature evolution of the X-band ESR spectra in a TDAE-C\textsubscript{60} single crystal for the two different crystal orientations.

Fig. 18 Temperature dependence of the intensity of the ESR signal for three different crystal orientations. Inset: the temperature dependence of the inverse ESR signal suggests antiferromagnetic correlations at high temperatures, which change to ferromagnetic ones close to $T_\text{C}$.
been noted that the obtained Curie temperature is negative (see for instance inset to Fig. 18), which was interpreted as a signature of antiferromagnetic correlations at high temperatures. Obviously these correlations somehow change their nature roughly below 50 K when they become predominantly ferromagnetic. A dramatic transition to the ferromagnetic state below 16 K is clearly visible as ESR intensity increases by two orders of magnitude. The low-temperature intensities are not quite the same for all three orientations, as the ESR signal intensity measured along the crystal $c$-axis is a factor of 3 smaller than the one measured along the crystal $b$-axis.

Another indication for the ferromagnetic transition is the shift of the ESR line. The center of the main “ferromagnetic” line strongly shifts with decreasing temperature. For $b \parallel H_0$ the center of the line shifts to lower fields (Fig. 19). The shift saturates below 10 K and amounts to 43 G at 5 K, while the linewidth is about 10 G at this temperature. For $a \parallel H_0$ the shift is in the opposite direction, i.e., to higher fields and amounts to 61 G at 4 K. The shift is again significantly larger than the linewidth, which is here of the order of 14 G. The shifts are nearly field independent, suggesting that this shift is due to the onset of internal fields and not due to the temperature dependence of the $g$-factor.

We have measured the frequency-field dependence of the ESR signal between 30 MHz and 245 GHz. At high fields (Fig. 20) this relation is nearly linear at $T=5$ K, i.e., well below the ferromagnetic transition temperature [105]. This may be at first glance surprising, as in the magnetically ordered phase one would expect a nonlinear resonance field–resonance frequency relation. The answer to that came only later on from low-field ferromagnetic resonance data discussed in the next section.
Fig. 20  Resonance field–resonance frequency relation in TDAE-C$_{60}$ at $T$=5 K and at high fields

Fig. 21  Temperature dependence of the electron spin–lattice relaxation time $T_{1e}$ in powdered TDAE-C$_{60}$
Interestingly one can – using a 90–180° pulse sequence – detect an echo ESR signal below 20 K [106, 107]. The echo intensity grows on cooling through the transition temperature, demonstrating the presence of magnetic field gradients below \( T_C \), which are absent above \( T_C \). The \(^1\text{H}\) and \(^{14}\text{N}\) hyperfine couplings on the TDAE\(^+\) ion were studied using electron spin echo envelope modulation (ESEEM) spectroscopy [107]. The frequency-domain spectrum, obtained by the Fourier transform of the time domain ESEEM signal, shows a complex multiline structure between 0.5 and 6 MHz arising from \(^{14}\text{N}–\text{C}_{60}\) coupling. The \(^{14}\text{N}\) peaks can be well reproduced by assuming two sets of triplets, corresponding to two different axially symmetric hyperfine coupling tensors. The existence of two \(^{14}\text{N}\) hyperfine couplings reflects the nonplanar structure of the TDAE\(^+\) ion in TDAE–C\(_{60}\). The isotropic \(^{14}\text{N}\) hyperfine coupling constants were determined to be 2.27 and 3.2 MHz, respectively. Other ESEEM lines were found in the vicinity of the \(^1\text{H}\) Larmor frequency: a central one at the proton Larmor frequency – showing no hyperfine coupling – and a doublet centered on the \(^1\text{H}\) Larmor frequency. These results demonstrate the presence of a very low but nonzero unpaired electron spin density on the TDAE\(^+\) ion.

The temperature dependence of the electronic spin memory time \( T_M \) was determined in powdered TDAE–C\(_{60}\) [106]. The memory time \( T_M \) is nearly temperature independent above \( T_C \) and is of the order of 30 ns. Below \( T_C \) it increases monotonically on cooling and reaches 92 ns at 4.2 K. No critical anomaly has been observed at \( T_C \). The spin–lattice relaxation time (Fig. 21) was found to coincide with \( T_M \).

### 4.2 Ferromagnetic Resonance

The explanation of the nature of the strong ESR signal of TDAE\(^+\)–C\(_{60}\) in the magnetically ordered phase came from the ESR measurements in low magnetic fields.

In view of the presence of strong exchange fields, electron spin resonance in ferromagnetic and antiferromagnetic systems, i.e., ferromagnetic resonance, is completely different from ordinary paramagnetic spin resonance. It represents a coherent precession of the entire magnetization or sublattice magnetization around the effective fields, and is in contrast to normal paramagnetic resonance characterized by a nonlinear dependence of the resonance frequency on the external field. The number of modes and the field dependence of the resonance frequencies allow for discrimination between ferromagnets, antiferromagnets, or spin-canted antiferromagnets [108]. The resonance frequency in magnetically ordered phases depends on the magnitudes of the exchange, anisotropy, and demagnetization fields [108]. The relationship between the resonance frequency and the resonance field becomes strongly nonlinear and is determined by the nature of the magnetic ordering. While in simple ferromagnets only one resonance mode is predicted, in antiferromagnets and weak ferromagnets two resonance modes should be found. For instance, for both uniaxial and weak ferromagnets, when the external magnetic field is perpendicular to the easy axis, a resonance mode with a dip in the resonance field–resonance frequency relation at a resonance field equal to the anisotropy field is found. However, in weak ferromagnets, an additional high-frequency antiferromagnetic-type mode is also present.
Clear evidence for the presence of a ferromagnetic resonance in TDAE-C$_{60}$ was found in the radio-frequency region [109]. The electron magnetic resonance spectra of a TDAE-C$_{60}$ single crystal at $H$ for $T < T_C$ show a single resonance line with no fine structure. With decreasing resonance frequency the resonance field at first monotonically decreases down to 110 MHz. Below that, for a given resonance frequency, two resonance fields were found. At 105 MHz the center of the high-field resonance is at 59 G and the center of the low-field resonance at 2 G. The higher resonance field decreases and the lower resonance field increases with decreasing resonance frequency until the two lines merge at 50 MHz. The resulting resonance frequency versus resonance field relation (Fig. 22) shows a zero field gap at 105 MHz and a dip at 29 G. This nonlinear behavior is characteristic of ferromagnetic resonance. At frequencies higher than 200 MHz the resonance frequency versus resonance field relation is linear (Fig. 22b), thus explaining the failure of earlier attempts to observe ferromagnetic resonance in this system [105]. The field–frequency relation is linear up to the L-band (1.2 GHz), as well as in the X-band (9.6 GHz) and Q-band (34 GHz). This is also true for the high-field ESR spectra at 94 GHz (Q-band) and 245 GHz. It should be stressed that no other resonance mode was detected in the low-field frequency range between 30 and 200 MHz for $H || H$. This rules out the existence of antiferromagnetic-type resonance (which is expected also in weak ferromagnets) where two resonance modes should be seen. The strongly nonlinear behavior (Fig. 22a) also eliminates the possibility of superparamagnetism.

Agreement between theory and experiment becomes quantitative, if the demagnetizing field effects are also taken into account. This leads to values of the anisotropy field, $H_K = 29$ G and the demagnetizing field, $H_{dem} = -39$ G. The nonlinear dependence of the resonance field on the resonance frequency disappears

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**Fig. 22a, b** Dependence of the resonance frequency on the resonance field ($a || H$) in a TDAE-C$_{60}$ single crystal a at $T=5$ K ($<T_C$) and b at $T=20$ K ($>T_C$)
above the transition temperature in the paramagnetic phase (Fig. 22b). Ferromagnetic resonance data thus indicate that the system can be described rather well by the easy axis Heisenberg model with a very small anisotropy field. This field is by a factor of $10^4$–$10^5$ smaller than the exchange field.

4.3 Muon Spin Relaxation

Very strong evidence for long-range magnetic order comes also from zero-field muon spin relaxation (ZF-$\mu^+$SR) experiments performed on TDAE-C$_{60}$ powder [110]. $\mu^+$SR spectroscopy is an extremely powerful technique in cases of small-moment magnetism and in all instances where magnetic order is of a random, very short range, spatially inhomogeneous, or incommensurate nature [111]. Nearly 100% spinpolarized $\mu^+$ are implanted into the solid sample and after they come to rest at an interstitial site, they act as highly sensitive microscopic local magnetic probes. In the presence of local magnetic fields, $\langle B_\mu \rangle$, they will precess with a frequency $\nu_{\mu} = (\gamma_{\mu}/2\pi) \langle B_\mu \rangle$, where $\gamma_{\mu}/2\pi = 13.55$ kHz/G. In the absence of an applied external field (ZF), the appearance of a precession signals the onset of an ordering (ferromagnetic or antiferromagnetic) transition. Moreover, application of a magnetic field parallel to the initial muon spin polarization (longitudinal field, LF) allows the decoupling of the $\mu^+$ spin from the static internal fields.

In well-annealed powdered TDAE-C$_{60}$, a heavily damped oscillating signal ($\nu_\mu = 0.92(2)$ MHz at 3.2 K) was observed in zero field (Fig. 23), providing definite proof of the existence of long-range magnetic order below 16.1 K. The strong muon spin relaxation – whose quasistatic nature was confirmed by LF measurements – found in ZF implies the presence of substantial spatial disorder and inhomogeneity effects. The local field distribution, $\langle \Delta B^2 \rangle^{1/2} = 48(2)$ G, is smaller than $\langle B_\mu \rangle = 68(1)$ G by only a factor of 1.4. In addition, the temperature dependence of $\nu_\mu$ (Fig. 24), which mirrors that of the magnetization at 100 G, follows Bloch’s $T^{3/2}$ law. Thus, it appears that spin wave (magnon) excitations

![Graph](image.png)

**Fig. 23** Evolution of the zero-field (ZF) $\mu^+$ spin polarization, $P_\mu(t)$, between 3.2 and 16.8 K for TDAE-C$_{60}$.
dominate the temperature dependence of the spontaneous magnetization, even at temperatures close to $T_C$. Alternatively, the magnon-like behavior may reflect a more complicated physical picture of the system, where the intrinsic orientational disorder associated with the fullerene molecules gives rise to a broad distribution of exchange constants (and ordering temperatures).

4.4 $^1$H NMR

NMR measurements in magnetic systems are simpler to interpret than the ESR measurements due to the fact that nuclear spins act as local probes of the internal magnetic fields. In this respect they are similar to $\mu^+$SR measurements. While in $\mu^+$SR one needs to implant $\mu^+$ into the crystal lattice ($\mu^+$ may also slightly distort the crystal structure and thus change the local magnetic properties, which are probed), in NMR experiments one uses nuclear spins of the inspected material itself. However NMR measurements have a much smaller signal-to-noise ratio than ESR and are usually done in very high magnetic fields of a few Tesla.

Two different nuclei in TDAE-C$_{60}$ have been investigated so far by NMR: protons of methyl groups of the TDAE molecule and $^{13}$C nuclei of the C$_{60}$ ion. The main difference between these two nuclei (in addition to their relative sensitivity) is that methyl protons experience mostly the dipolar fields of the C$_{60}$ magnetic moments. On the other hand $^{13}$C nuclei on each C$_{60}$ ion will, in addition to dipolar fields, also feel the hyperfine contact field of the unpaired electron spin. Details of the $^{13}$C NMR results will be given in the next section. Here we
just briefly summarize the $^1$H NMR results on powdered TDAE-$C_{60}$ as well as on single crystals of TDAE-$C_{60}$.

In powdered TDAE$^+$-$C_{60}$ we found [112] at room temperature and $\omega_1/2\pi = 270$ MHz two proton NMR lines, $A$ and $B$, of nearly equal intensity (Fig. 25). The position of the $A$-line is nearly temperature independent whereas the position of the $B$-line (Fig. 26) follows a Curie–Weiss law – with a negative Curie temperature down to $T_C$. Please note that the same observation about the negative Curie-
Weiss temperature came out from ESR measurements too. Below $T_C$ the measurements were not reliable any more as part of the $B$-line could be lost in the noise. The simplest explanation is that the $B$-line belongs to the ferromagnetic and the $A$-line to the nonferromagnetic modification of TDAE-C$_{60}$.

The transformation between the two modifications, i.e., $\alpha$ and $\alpha'$ modifications, is in TDAE-C$_{60}$ single crystals much slower than in powdered samples. This fact has enabled the study of the individual properties of the ferromagnetic [113] and nonmagnetic modifications, respectively, as well as the difference between the two modifications [114]. While in powder samples the intensities of the methyl proton $A$- and $B$-lines are nearly equal at room temperature this is not always true in single crystals. On the other hand in the nonmagnetic $\alpha'$ samples, at room temperature the intensity of the line $B$ (i.e., the line which shows a paramagnetic frequency shift following a Curie–Weiss law) is much weaker than the intensity of the $A$-line. With temperature cycling between 200 and 330 K one can change the relative intensities of the two lines [115]. This most probably reflects the annealing process that transforms single crystals from the $\alpha'$ to $\alpha$ modification.

With decreasing temperature both the $A$- and $B$-lines broaden and the linewidth of the $B$-line increases to 25 kHz at 170 K. This is the temperature range where the rotational motion of the C$_{60}$ ion freezes out, as we shall see from the $^{13}$C NMR experiment. The protons are thus also sensitive to orientational ordering of the C$_{60}$ ions through the coupling of the methyl protons with the unpaired electron at the C$_{60}$ site. At 50 K the halfwidth of the $B$-line is already about 250 kHz.

Fig. 27 $^1$H NMR spectra of TDAE-C$_{60}$ single crystal at some representative temperatures in the vicinity of the magnetic transition.
Below $T_C$, in ferromagnetic-type TDAE-C$_{60}$ single crystal samples, the proton NMR spectra are several MHz broad (Fig. 27), and the B-line is shifted with respect to the A-line. As already noted for the powder samples, the intensity of the B-line slowly decreases with decreasing temperature below $T_C$ and the intensity of the A-line increases – most probably at the expense of the B-line. The disappearance of the B-line indicates that at low temperatures the mechanism for spin cancellation is most probably enhanced spin pairing taking place in TDAE$^+$ ions. As we shall see later from the $^{13}$C NMR measurements this mechanism may be promoted by the orientational ordering of JT-distorted C$_{60}$ ions. The A-line also approaches a double-peaked lineshape at $T$=5 K, which is in agreement with the spin-pairing mechanism into a singlet-like state. If the ground state of the A-line is either a spin or charge density wave, the amplitude of the density wave should be very small since the shifts of the two peaks of the A-line are rather small as compared with the shift of the magnetic B-line. Still another possibility for the decreases of the intensity of the ferromagnetic B-line at low temperatures would be a gradual disordering of the perpendicular orientations of the distortion axes of neighboring Jahn–Teller-distorted C$_{60}$ ions.

4.5 $^{13}$C NMR

The lineshape of the $^{13}$C NMR spectra contains the information about the orientational order of the C$_{60}$ molecules. On the other hand the shift of the $^{13}$C lines measures the magnitude of the local magnetic fields. Here we wish to briefly describe the low-temperature behavior of well-annealed TDAE-C$_{60}$ leading to the ferromagnetic transition at $T_C$=16 K and then to an inhomogeneous ferromagnetic state below $T'$=10 K. The transition may be associated with the fact that the two different orientational states of the C$_{60}$ ions have slightly different energies. Therefore one state starts to disappear at low temperature leading to an increase in orientational disorder and a decrease in the effective ferromagnetic coupling and local magnetization.

The $^{13}$C NMR spectra of a 40% $^{13}$C-enriched well-annealed TDAE-C$_{60}$ powder sample (Fig. 28) were measured at a magnetic field $H_0$=9 T above and below $T'$=10 K [119]. The fact that this is the only $^{13}$C line from the C$_{60}$ ion in TDAE-C$_{60}$ has been proved by the measurement of the frequency-swept spectra in the range of 10 MHz around the $^{13}$C Larmor frequency at $H_0$=6.34 T. The TDAE $^{13}$C line is not seen, as its intensity is about three orders of magnitude smaller than the C$_{60}$ line since the sample was not $^{13}$C enriched at the TDAE sites. On cooling we found a $^{13}$C linewidth transition around 150 K connected with the gradual freeze-out of the C$_{60}$ molecular motion [91]. The difference between the transition temperature of 180 K seen by ESR reflects the different time scales of these two techniques. In the ferromagnetic phase, which in a magnetic field of 9 T starts around 25 K and not at 16 K as in zero magnetic field, the width of the $^{13}$C NMR spectra first decreases with decreasing temperature below $T_C$ (Fig. 29 a). In the same temperature interval the center of the $^{13}$C NMR line starts to shift to higher frequencies (Fig. 29b) by about 40 kHz, indicating an increase in the average internal field with decreasing temperature. Around $T'$=10 K we find a sudden
and huge increase in the $^{13}$C NMR linewidth. The inhomogeneous $^{13}$C frequency distribution $f(\nu) = dN/\nu$ is here nonzero over a region of nearly one MHz. At the same temperature we also observe a dramatic change in the $^{13}$C NMR lineshape. Although it is difficult to measure changes in the center of the frequency distribution below $T'$, we note that the position of the center of the $^{13}$C NMR line saturates at $T'$ or even slightly shifts to lower frequencies by 5–10 kHz relative to

**Fig. 28** Typical $^{13}$C NMR spectra measured in TDAE-C$_{60}$ (upper row). Simulations of the $^{13}$C NMR spectra assuming: fast isotropic rotations of C$_{60}$– ion at 250 K; static C$_{60}$– ions but fast pseudorotations of the Jahn–Teller distortion axes at 50 K; and the completely static case at 5 K (bottom row)

**Fig. 29a, b** Temperature dependence of a the $^{13}$C NMR linewidth and b the center of the $^{13}$C NMR line in $^{13}$C-enriched TDAE-C$_{60}$
the $^{13}$C NMR Larmor frequency with decreasing temperature. This demonstrates a saturation or marginal reduction in the effective internal magnetic field with decreasing temperature below $T'$. We would also like to point out that the evolution of the internal magnetic field distribution measured for instance by µSR [110] cannot account for this huge $^{13}$C NMR line broadening. We have found that the internal field distribution at 4 K is about 48 G. In the $^{13}$C NMR frequency this would correspond to about 50 kHz, i.e. more than an order of magnitude less than it has been observed. In addition we have not observed such anomaly at 10 K in µSR measurements. To explain this surprising broadening deep in the ferromagnetic phase one thus needs a more radical solution. As we shall show later this is due to the change of the electron-nuclear hyperfine interactions as the dynamics of the JT pseudorotations slows down below $T'$.  

4.6 Magnetic Properties of TDAE-$C_n$ with $n$>60

In contrast to TDAE-C$_{60}$ no magnetic transition has been observed in the related compound TDAE-C$_{70}$ or other higher fullerene salts [116, 117]. This system shows a paramagnetic behavior in the susceptibility $\chi=C/T$ down to 4 K [116]. The intensity and shape of the room temperature X-band ESR spectrum of TDAE-C$_{70}$ are, on the other hand, nearly the same as in TDAE-C$_{60}$, demonstrating the presence of one-electron transfer from the TDAE molecule to the C$_{70}$ molecule, similar to TDAE-C$_{60}$. The temperature dependence of the X-band ESR spectra of powdered TDAE-C$_{70}$ has been studied by Tanaka et al. [116, 117] and revealed no anomalous shift or broadening of the ESR line down to 4 K. The $g$-factor is at room temperature significantly higher ($g=2.0023$) than the corresponding one in powdered TDAE-C$_{60}$ ($g=2.0003$). Similar to TDAE-C$_{60}$, no separate TDAE$^+$ ESR signal has been detected.

The high-field ESR and the $^1$H NMR spectra have been measured on powdered TDAE-C$_{70}$ [118]. The temperature evolution of the ESR spectra measured at a Larmor frequency of 245 GHz is shown in Fig. 30. A single narrow line has been observed at temperatures between room temperature and 150 K. However below 150 K another line appears at the low-field side of the main ESR line. This line has not been observed in the X-band ESR spectra. Whereas the position of the main high-field ESR line is temperature independent between room temperature and 4 K, the low-field line shows strong temperature dependence and exhibits a shift of 4.2 mT to lower fields between 50 and 4 K. We have suggested [118] that this is due to the occurrence of a magnetic field-induced short-range magnetic order in TDAE-C$_{70}$ which cannot fully develop into long-range magnetic order. However we note that it can also be due to the presence of two different $g$-factors in this compound as a result of a Jahn–Teller effect. In such a case the Jahn–Teller distortion should be static on the high-field ESR time scale, similar to the case of (P(C$_6$H$_5$)$_4$)$_2$C$_{60}$I [48].

A significant difference between TDAE-C$_{60}$ and TDAE-C$_{70}$ is also seen in the 270-MHz proton NMR spectra at 6.3 T. In powdered TDAE-C$_{70}$ only a single proton resonance line of super-Lorentzian shape is observed at room temperature,
whereas two well-resolved proton NMR lines (A and B) are seen in powdered TDAE-C60. The position of the proton line observed in TDAE-C70 is independent of temperature and intermediate between the A- and B-lines in TDAE-C60. The proton second moment in TDAE-C70 nearly continuously increases with decreasing temperature, similar to TDAE-C60. The magnitude of the proton second moment shows that it is due to proton–electron dipolar coupling and not due to purely nuclear–nuclear dipolar interactions. This shows that all methyl protons in TDAE-C70 feel the electronic dipolar local field but not the hyperfine contact Fermi field.

5 The Impact of the Jahn–Teller Effect on Magnetism in TDAE-C60

Detecting the Jahn–Teller distortion at low temperatures and the corresponding charge redistribution on individual C60 ions is far from trivial, mostly due to the very small distortion and the fact that there can be many competing configurations involved. However, very recently we have found a way to study the Jahn–Teller effect in TDAE-C60 by using the 13C NMR technique [119, 120]. The observation of this effect in TDAE+C60 is made possible by the changes in the Fermi contact electron–nuclear coupling shifts of the 13C NMR lines which accompany the Jahn–Teller distortion and act as a magnifying glass, making the minute Jahn–Teller distortions and the resulting redistribution of the unpaired electron density visible in the 13C NMR spectra. The Fermi contact coupling is nonzero in view of the s-wave admixture into the p-type unpaired electron spin wave function. The results obtained allow for a quantitative determination of the belt-like unpaired electron spin density distribution around the elongated C60 ions, which is responsible for the relatively high ferromagnetic transition temperature in this purely organic ferromagnet. The technique can also be used in other

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**Fig. 30** The temperature dependence of the high-field ESR spectra of powdered TDAE-C70. Here the Larmor frequency is 245 GHz
doped fullerenes exhibiting a Jahn–Teller effect, which is static on the NMR time scale.

The positions of the $^{13}$C NMR lines in $^{13}$C$^\pm$ ions are mainly determined by the Fermi contact electron–$^{13}$C nuclear coupling

$$H_{Hf} = \sum_{ij} \vec{I}_i \cdot A_{ij} \cdot \vec{S}_j$$

Here $\vec{I}_i$ is the $^{13}$C nuclear spin, $\vec{S}_j$ is the unpaired electronic spin, and $A_{ij}$ is the Fermi contact hyperfine coupling tensor. This coupling is identical for all $^{13}$C nuclei as long as the C$_{60}$ ion is spherical, but becomes different for different nuclei after the Jahn–Teller distortion leading to an inhomogeneous frequency distribution. The homogeneous width of the $^{13}$C NMR lines is, on the other hand, mainly determined by the electron–nuclear dipolar interaction

$$H_{dd} = \sum_{j,k} \frac{\hbar^2 Y_e^2 Y_C^2}{r_{ij}^3} \left( \vec{I}_j \cdot \vec{S}_i - 3 \left( \frac{\vec{I}_j \cdot \vec{r}_{ij}}{r_{ij}^3} \right) \cdot \left( \frac{\vec{S}_i \cdot \vec{r}_{ij}}{r_{ij}^3} \right) \right)$$

where $Y_e$ and $Y_C$ are the electronic and $^{13}$C nuclear giration ratios, respectively, and $\vec{r}_{ij}$ is the vector connecting the $^{13}$C site and the unpaired electronic position. In view of the small magnitude of the Jahn–Teller distortions, the electron–$^{13}$C dipolar interaction is not significantly affected by the Jahn–Teller effect. The same is true for the contribution to the $^{13}$C NMR linewidth of the anisotropic $^{13}$C chemical shift tensor $H_{CS} = \sum_j I_j \cdot \sigma_j \cdot \vec{B}_0$, which is minor compared to the electron–nuclear contact coupling.

To a rather good approximation we can assume that all three above-mentioned electron–$^{13}$C coupling tensors are axially symmetric and that the sum of their contributions determines the components of the shift tensor $\mathbf{K}$. In this case the shape of the $^{13}$C NMR spectrum depends on the values of the $^{13}$C shift tensor $K_{\perp}$ and $K_{\parallel}$ is the component of the $^{13}$C shift tensor normal, while the component $K_{\perp}$ is tangential to the C$_{60}$ surface. In the static limit, the $^{13}$C NMR frequency is given by [120, 121]

$$v_R(\Theta_B, \varphi_B, \vartheta_B, \varphi) = v_L [K_{\parallel}^0 + Bp(\vartheta) + (K_{\parallel}^0 - K_{\parallel}^0) \cos^2 \Theta]$$

where $\Theta$ is the angle between the direction of the external magnetic field and the largest principal axes of the shift tensor. $\Theta$ can be expressed as

$$\cos \Theta = \sin \Theta_B \sin \vartheta \cos(\varphi - \varphi_B) + \cos \Theta_B \cos \varphi$$

where $\Theta_B, \varphi_B$ describe the orientation of the magnetic field with respect to the crystal lattice and $\Theta, \varphi$ describe the position of a given C atom on the C$_{60}$ ion (Fig. 31). It is assumed that the deviation $p(\vartheta)$ of the distribution of the unpaired electron spin density from a C$_{60}$ spherical symmetry modifies the parallel and perpendicular components of the anisotropic shift tensor $\mathbf{K}$ by the same amount.

$$\delta K_{\parallel,\perp} (\vartheta,t) = Bp(\vartheta,t).$$

At very low temperatures it is reasonable to assume that the Jahn–Teller distortion is static, so we can ignore the time dependence of the charge distribution.
function. The $^{13}$C NMR spectrum is then calculated by performing powder averaging taking into account all possible $^{13}$C sites on the $C_{60}$ sphere

$$f(v) = \left[ \left( \left[ \left( \left[ \left| \delta[v - v(\vartheta_B, \varphi_B, \theta, \phi)] \right] \sin \vartheta_B \right) d\vartheta_B \right) d\varphi_B \right) d\theta d\phi \right]. \tag{9}$$

Various different charge distribution functions were tested to fit the $T=5$ K spectrum. Basically we divide them into functions where the excess of charge is on the poles of the $C_{60}$ molecule, and into functions where the maximum charge density is on the equator of the $C_{60}$ ion (Fig. 32a, b). Typical representatives of these two classes are $p_1(\vartheta) = \frac{1}{3} - \cos^2 \vartheta$ and $p_2(\vartheta) = \cos^2 \vartheta - \frac{1}{3}$, respectively (Fig. 32b). Please note that the charge distribution functions were chosen in such a way that on the average $\langle p(\vartheta) \rangle = 0$, i.e., $p(\vartheta)$ describes only the deviation from the spherical charge distribution. In the high temperature limit one expects that the axes of Jahn–Teller distortion will flip/rotate fast on the $^{13}$C NMR time scale so that $\langle \delta K_{\perp(\vartheta)} \rangle (\vartheta, t) = 0$.

Examples of calculated $^{13}$C NMR spectra for Jahn–Teller-distorted $C_{60}$ ions for the two different charge distributions $p_1(\vartheta)$ and $p_2(\vartheta)$ are shown in Fig. 32c,d for a typical value of the parameter $B$. The spectra of the two cases are very different allowing for a clear discrimination between them. When most of the unpaired spin density is on the poles, the $^{13}$C NMR lineshape is very anisotropic with a lineshape roughly resembling a powder-like spectrum. On the other hand, the expected $^{13}$C NMR spectra for a maximum charge distribution on the equator is nearly triangular and much more symmetric.

Typical $^{13}$C NMR spectra measured in TDAE-$C_{60}$ are shown on the first row of Fig. 28. At high temperatures the $^{13}$C NMR line is very narrow and has an approximately Lorentzian lineshape. This indicates fast and nearly isotropic rotations of the $C_{60}$ ions effectively averaging out all anisotropic interactions. Isotropic contact interaction is of course still present and is about 40 ppm (the room-temperature shift of the $^{13}$C NMR line with respect to TMS is 188 ppm and the chemical shift is about 145 ppm), which is comparable with the shifts mea-

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**Fig. 31** Definitions of angles $\vartheta_B, \phi_B$, which describe the orientation of the magnetic field with respect to the crystal lattice and angles $\vartheta, \phi$ describing the position of a given C atom on the $C_{60}$ ion.
sured in other charged fullerenes. A large broadening of the $^{13}$C NMR line is observed on cooling. It occurs in two steps. First a large broadening occurs below 150 K, and we identify this as a temperature where a typical correlation time for a molecular rotation of the C$_{60}^-$ ion becomes comparable with the $^{13}$C NMR time scale. For a detailed discussion of the rotational dynamics of C$_{60}^-$ ions please see [121]. The $^{13}$C NMR lineshape takes a typical powder-like lineshape (see $^{13}$C NMR spectrum at 50 K in Fig. 28). On further cooling another drastic broadening is observed at 10 K. It seems that at $T_C=16$ K the $^{13}$C NMR linewidth first slightly shrinks and then, at much lower temperature $T'=10$ K, it increases by almost an order of magnitude. Surprisingly the lineshape also gradually changes and becomes very symmetric at $T=5$ K. A comparison with the theoretically calculated $^{13}$C NMR spectra shown in Fig. 32 clearly rules out the possibility that the charge density is distributed on the poles of the Jahn–Teller-distorted C$_{60}^-$ molecule. It is, however, compatible with the fact that the unpaired electron spin density distribution is located mainly on the equator of the molecule. We would like to point out here that the details of the distribution $p(\theta)$ may be slightly different from the one described here. This is due to the fact that a powder sample and not a single crystal has been used.

Let us now try to explain the observed lineshape and the large broadening at $T'=10$ K. In the temperature range between 10 and 50 K the C$_{60}^-$ ion by itself is static, i.e., it does not perform any sort of physical reorientation. However, the orientation of the Jahn–Teller distortion may change on a time scale comparable to the inverse $^{13}$C NMR linewidth, i.e., $\tau=1/\Delta\nu=3$ ns. A possible sequence of such pseudorotations between (symmetry allowed) competing orientations of the Jahn–Teller distortion are shown in Fig. 33. Molecular orbital calculations

![Diagram](image-url)
have been performed for $\text{C}_{60}$ Jahn–Teller distortions with $D_{3d}, D_{5d}$ and $D_{2h}$ symmetry. In view of the presence of the orthorhombic crystal field acting on the $\text{C}_{60}$ site in TDAE-$\text{C}_{60}$, one may expect that the $D_{2h}$ distortion is the most stable. In such a case the symmetry group of the distorted phase will be $P\bar{1}$ instead of $C2/c$, which is the symmetry group of nondistorted TDAE-$\text{C}_{60}$. One may thus reasonably expect that one orientation of the axis of the Jahn–Teller distortion, which is aligned along the crystal $c$-axis, is preferable over the two perpendicular ones. At low temperatures the $\text{C}_{60}$ ions in TDAE-$\text{C}_{60}$ preferably (although not 100%) freeze into these two orientations. If the Jahn–Teller distortions are cooperative, neighboring $\text{C}_{60}$ ions at $T_c$ freeze out in such a way that their distortions are...

Fig. 33 A schematic picture showing the Jahn–Teller pseudorotations between three mutually perpendicular distortion directions in TDAE-$\text{C}_{60}$

Fig. 34 Temperature dependence of $\tau_{JT}$ as determined from the fits of the $^{13}$C NMR lineshape in TDAE-$\text{C}_{60}$. The solid line is a guide to the eye
tion axes are perpendicular to each other leading to ferromagnetic couplings (see Fig. 13). Since these two orientations may have slightly different energies, one orientation may start to disappear at low temperatures leading to increased disorder. As the temperature rises one orientation of the Jahn–Teller distortion may transform into the second, and vice versa, bringing dynamics into the otherwise “static” $^{13}$C NMR spectra. Thus, although the position of the $^{13}$C nuclei does not change significantly (as the Jahn–Teller distortion is very small) during this transformation, the charge density distribution on C$_{60}^-$ ions – and as discussed also the $^{13}$C NMR frequency – may change dramatically. Effectively we thus have a problem of a multisite exchange where the resonant frequency of $^{13}$C nuclei jumps between several different values corresponding to different orientations of the axis of Jahn–Teller distortion (Fig. 33).

The temperature dependence of the correlation time for the Jahn–Teller pseudorotation $\tau_{\text{JT}}$ obtained by fitting the $^{13}$C NMR lineshapes [121] is shown in Fig. 34. Although in the present model the unpaired spin density on individual C$_{60}^-$ ions may be only qualitatively correct, this will only slightly affect the temperature dependence of the $\tau_{\text{JT}}$.

6 Conclusions and Future Prospects

In conclusion we may say that all the experimental and theoretical investigations of TDAE-C$_{60}$ point to a close correlation between the spin and the orientational ordering of Jahn–Teller-distorted C$_{60}^-$ ions. Slowing down of the Jahn–Teller pseudorotations starts in the vicinity of the ferromagnetic transition and is never really completed. From our NMR work we can deduce that the Jahn–Teller-determined orbitals remain, at least on the $^{13}$C NMR time scale, disordered down to 10 K forming a sort of “orbital liquid” state. However below $T=10$ K we find a significant slowing down of the Jahn–Teller pseudorotational dynamics leading to “orbital ordering”.

Whether the orbital ordering is a cooperative phenomenon in TDAE-C$_{60}$ or not still remains an open question. If it is a cooperative phenomenon, one can indeed apply the approach of Asei et al. [122] with a starting Hamiltonian

$$H = -\sum J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum g_{ij} \vec{S}_i \vec{S}_j O_i O_j + \sum I_{ij} O_i O_j.$$  \hspace{1cm} (10)

Here $O_i$ is the isospin describing the C$_{60}^-$ orbital, $I_{ij}$ is the orbital exchange constant, and $J_{ij}$ is the Heisenberg spin-exchange constant. This Hamiltonian can describe many of the magnetic properties of TDAE-C$_{60}$.

If there is no cooperative orbital ordering, the appropriate Hamiltonian which describes such a system is

$$H = J_{\perp} q(T) \sum \vec{S}_i \cdot \vec{S}_j + J_{||} (1 - q(T)) \sum \vec{S}_i \cdot \vec{S}_j.$$  \hspace{1cm} (11)

In this Hamiltonian $J_{\perp}$ and $J_{||}$ are the exchange interactions corresponding to the orthogonal or perpendicular orientations of the two Jahn–Teller-distorted C$_{60}$ ions. Most likely $J_{\perp}$ is of ferromagnetic character and $J_{||}$ is of antiferromagnetic character. $q(T)$ is simply the probability of finding the two distorted molecules
in mutual orthogonal orientations. This Hamiltonian is reminiscent of the random-exchange Hamiltonian first introduced by Soos et al. [123].

Still another model has been proposed by Narymbetov et al. [86]. The magnetic behavior of the TDAE-C_{60} is here modeled in terms of a Hamiltonian for a noninteracting two-level system, where the coupling between configurational and magnetic degrees of freedom is introduced by the dependence of the exchange interaction \( J \) on the relative concentration \( x \) of configurations favoring a ferromagnetic exchange interaction. This Hamiltonian can be written as

\[
H = -\sum_{ij} J_{ij}(x) \vec{S}_i \cdot \vec{S}_j + \Delta \sum_i (\sigma_i^z + \frac{1}{2}).
\]  

(12)

Here \( \Delta \) is the energy difference between the two configurations, \( \vec{S} \) is the spin operator, and \( \sigma^z \) is the orbital operator describing the two \( C_{60} \) configurations. A spontaneous magnetization appears when the concentration \( x = \langle \sigma^z + \frac{1}{2} \rangle \) is larger than a critical value. This can be understood in terms of a percolation threshold for the existence of an infinite magnetic cluster. When the magnetic energy exceeds the configurational energy difference, a ferromagnetic phase is stable below \( T_C \). If on additional lowering the temperature \( x \) falls below the critical value, a nonmagnetic phase could appear at low temperatures.

Further experiments are needed to see which of the above models corresponds to the reality in TDAE-C_{60}. At the moment we still cannot definitely exclude any of them. Nevertheless it is clear that Jahn–Teller distortions of the \( C_{60} \) ions and the interplay between orientational and spin ordering is essential for the occurrence of organic ferromagnetism in TDAE-C_{60}.

The following “general” conclusions about the magnetism in \( C_{60} \)-based compounds can thus be made. First, a static Jahn–Teller distortion is responsible – and needed – for the occurrence of the long-range magnetic order in TDAE-C_{60}. The noncubic environment favors some orientations of the distortion axes against the others. A very special arrangement of the Jahn–Teller-distorted \( C_{60} \) ions in TDAE-C_{60} – most probably consisting of chains of \( C_{60} \) ions with mutually perpendicular distortion axes – leads to ferromagnetic ordering at low temperatures. If on the other hand the arrangement of \( C_{60} \) ions is slightly different, other magnetic ground states, such as the antiferromagnetic one, can occur. We note that (NH\(_3\))K\(_3\)C\(_{60}\) has a face-centered orthorhombic cell and an antiferromagnetic spin ordering [124]. Neutron diffraction experiments revealed orientational ordering of the \( C_{60} \) units, which adopt two different orientations related by a 90° rotation around the \( c \) orthorhombic axis and order along the \( a \)-axis [125, 126]. (NH\(_3\))K\(_3\)C\(_{60}\) makes a transition to an insulating antiferromagnetic ground state below \( T_N = 36.5 \) K [127, 128]. It may well be that the main difference between TDAE-C\(_{60}\) and (NH\(_3\))K\(_3\)C\(_{60}\) is a difference in the packing of Jahn–Teller-distorted \( C_{60} \) ions in the crystal structure. Reinvestigation of the low-temperature \(^{13}\)C NMR spectra of (NH\(_3\))K\(_3\)C\(_{60}\) [127, 129] might shed some additional light on this problem.

To search for new magnetic materials in \( C_{60} \)-based charge-transfer systems, one needs to look for cases where Jahn–Teller-distorted orientationally ordered \( C_{60} \) ions occupy noncubic sites. It would be very interesting to test the magnetic properties of doped smaller fullerides, i.e., \( C_n \) with \( n \leq 60 \), as one expects larger exchange couplings in these systems. Another direction would be to search
among polymerized C$_{60}$ systems. We note that this search already paid off with the discovery of Makarova et al. [130] that rhombohedral polymerized C$_{60}$ exhibits ferromagnetism even at room temperature. The Curie temperature for this system has been determined to be around 500 K. We are convinced that new magnetic materials based on C$_{60}$ will be found along these lines.

7

References