Metallicity in fullerides

Katalin Kamarás and Gyöngyi Klupp

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Metallic salts formed from fullerenes became popular because of their superconducting properties with a relatively high transition temperature, and were initially regarded as conventional metals and superconductors. Recently, owing to improved synthetic methods and a renewed interest in the study of their physical properties, many of them were found to exhibit exotic metallic and superconducting phases. In this paper, we summarize earlier results on unconventional metallic fulleride phases as well as the newly discovered extended fulleride superconductors. The proximity of the Mott transition, a typical solid-state effect, results in molecular crystals, where molecular spectroscopic methods prove very successful. We concentrate on infrared and optical spectroscopy which is very well suited to follow metallicity and phase transitions in this class of substances.

1 Introduction

Fullerenes were discovered more than 25 years ago, yet keep scientists fascinated ever since. Their simplicity and symmetry, coupled with their versatility enables them to be used as examples for many concepts in condensed matter physics, mainly related to electronic instabilities as electron correlations and superconductivity. As many new members of the family are emerging, due to sophisticated chemical preparation methods, they can be used to illustrate phenomena as correlated metallic and insulating behavior, the coexistence of superconductivity and electron correlations, and even non-conventional superconductivity. Here we review recent developments in this direction, concentrating on the metallic/non-metallic character in the normal state. The family of fullerenes is in itself a vast one, but we restrict the topic to its prime example, the C_{60} molecule and its molecular anions. (Therefore, throughout the paper, the term "fullerene" means strictly C_{60}.) This paper is not meant to be a comprehensive review since such already do exist. Many of the instabilities have been discussed on the experimental side by Forró and Mihály and theoretically by Capone et al. The properties of fulleride salts of alkali and alkaline earth metals were presented in a unified framework by Iwasa and Takenobu. Following the first discoveries of superconductivity in alkali fullerenes, the general assumption was to regard them as simple metals, turning to Bardeen–Cooper–Schrieffer (BCS) superconductors below the transition temperature; in this sense, they were regarded "less interesting" than inorganic, for example cuprate, superconductors. This view was not shared by the whole community; even in the early days of fullerene research, other explanations were put forward, and as, thanks to innovative chemistry, more and more fulleride salts with sufficient purity have been synthesized, the signs are pointing towards novel mechanisms in both metallicity and superconductivity. We try to present an overview of these results and put them in perspective to show why we think fullerides, similarly to cuprates and organic conductors, are ready to take their place as model compounds for these mechanisms.

We adopt the point of view of the molecular spectroscopist, which has proven surprisingly useful when extended towards a more general condensed-matter approach.

2 Electronic structure

Metallic fulleride salts are composed of fulleride ions and cations, in most cases alkali or alkaline earth metal ions. To a first approximation, the latter act simply as electron donors to the fullerene molecules and the molecular ions can be regarded as the lattice sites providing the electrons that in turn form the band structure of the solid. The charge of these ions depends on the chemical composition, i.e. the charge donated by the cations per fullerene ball, the electronic properties are therefore largely determined by the composition.

The first Hückel calculation of the electronic structure of C_{60} by Haddon is still a very good starting point to qualitatively understand the situation in fulleride salts. The sequence and population of the C_{60} molecular orbitals (Fig. 1) resembles that of atomic orbitals with increasing angular momentum quantum number L. However, to regard the fullerene molecule as a simple atomic core is grossly oversimplified; instead, it is truly a chemical entity capable of molecular distortions and chemical reactions. The icosahedral, instead of...
spherical, symmetry causes the removal of degeneracy in the levels analogous to $L > 3$. The splitting relevant for the HOMO and LUMO levels is that of the $L=5$ level, containing 11 states, into $h_u$, $t_{1u}$, and $t_{2g}$ orbitals corresponding to the irreducible representations of the icosahedral point group $I_h$. Simple electron counting yields that the $h_u$ level will be the HOMO containing ten electrons, and the LUMO and LUMO+1, respectively, will be able to accommodate six electrons each. Based on the molecular results, Saito and Oshiyama calculated the band structure of $C_{60}$ and found it to be an insulator with a 1.5 eV direct bandgap. In this approximation, the HOMO band is based on the five $h_u$ levels and the LUMO band on the three $t_{1u}$ levels, with bandwidths around 0.5 eV. Adding electrons to a $C_{60}$ molecule and building up a solid from it results in a very similar band structure where the conduction band is partially filled (Fig. 1 illustrates the case for a solid built from trivalent fulleride ions). The band structure calculations based on the molecular orbitals give a very good starting point for the discussion of optical spectra. The direct transition between the HOMO and the LUMO is optically forbidden, but as soon as the LUMO becomes populated by electron doping, the LUMO $\rightarrow$ LUMO+1 transition will become allowed and show up around 1.1 eV. Higher-energy transitions in the optical spectra do not show significant changes compared to $C_{60}$.

The $t_{1u}$ LUMO band can accommodate up to six electrons and the results of the first experiments of doping $C_{60}$ with alkali metals showed that the highest concentration corresponds to $A_6C_{60}$. In the band picture of Fig. 1, when the LUMO-based band is partially filled, electrons have empty states to occupy in reciprocal space, meaning that they can propagate freely in real space (i.e., they cannot be assigned to any particular ionic core). An insulating state occurs if the band is either empty or completely filled; this is called a band insulator. Already at the time of discovery of conducting fullerides, it was noted that the simple band picture yielded an unphysically short mean free path (shorter than the inter-fulleride distance). In such cases, instead of the band model, another one is used where the electrons are confined to the molecular ions, and move between them by “hopping”. If the Coulomb repulsion between the electron and the nearest neighbor is too large, then it will prohibit hopping and the system will become an insulator despite the partial band filling in the band picture. Such a system is called a Mott insulator and the change between metallic and insulating behavior a Mott transition.

The concept of a Mott insulator is indeed easy to grasp for a chemistry-trained mind. We start with a solid consisting of molecular ions, each keeping its electrons in its vicinity. If we move these ions closer to each other, the overlap between the electron clouds increases until a collective electron system is formed and the crystal turns into a metal. The intermolecular distance can be tuned by external pressure or by “chemical pressure” i.e., decreasing the size of the counterion and thereby the lattice constant. In condensed matter physics, the parameters used in this model are the on-site Coulomb repulsion a precise stoichiometric composition, and not quite analogous to doping of semiconductors; however, because of the widespread usage of the term in the literature of fullerenes, we will use it in this sense here.

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**Fig. 1** The electronic structure of $C_{60}$ and the band structure of $A_3C_{60}$ after Hebard. Reproduced from Ref. 5 (http://journals.aps.org/rmp/abstract/10.1103/RevModPhys.68.855). Copyright (1996) by the American Physical Society.
molecule. The atoms above the plane of the paper are black while those under it are grey. (b) The two "standard orientations" of fulleride ions in a crystal where the principal crystal axis coincides with one of the molecular $C_5$ axes. Static or dynamic average of these two orientations with $D_{2h}$ symmetry results in overall tetragonal ($D_{4h}$) structure. Reproduced from Ref. 15 (http://journals.aps.org/prb/abstract/10.1103/PhysRevB.73.085415). Copyright (2006) by the American Physical Society.

Fig. 2 (a) Possible symmetry-lowering distortions in fulleride ions: $D_{5d}$, $D_{3d}$ and $D_{2h}$. The axis along which the distortion occurs is perpendicular to the plane of the paper through the center of the molecule. The atoms above the plane of the paper are black while those under it are grey. (b) The two "standard orientations" of fulleride ions in a crystal where the principal crystal axis coincides with one of the molecular $C_5$ axes. Static or dynamic average of these two orientations with $D_{2h}$ symmetry results in overall tetragonal ($D_{4h}$) structure. Reproduced from Ref. 15 (http://journals.aps.org/prb/abstract/10.1103/PhysRevB.73.085415). Copyright (2006) by the American Physical Society.

An additional complication arises because here the "cores" are not atoms, but molecules. The icosahedral cage, consisting of sixty atoms forming one of the most symmetric shapes found in nature, is inherently sensitive to symmetry-lowering effects. (These play a much less important role in other organic conductors and superconductors, where the complicated organic molecules form crystals with very low symmetry.) The primary effect is the crystal field, determined by the arrangement of the counterions. If the symmetry of the crystal is lower than cubic, the degeneracy of the $t_{1u}$ orbitals is lifted and the partially occupied orbitals can become full. The symmetry lowering and the resultant splitting of the triply degenerate $t_{1u}$ levels is determined by the largest common subgroup of the icosahedral group and the space group of the crystal. Possible axes of molecular distortion into the three subgroups $D_{5d}$, $D_{3d}$ and $D_{2h}$ are indicated in Fig. 2(a). The distortions consist of elongation or compression along these axes. Figure 3 illustrates the splitting for possible high-symmetry crystal structures. It is worth noting that there occurs a threefold splitting in tetragonal crystals, a consequence of the lack of a fourfold axis in icosahedral symmetry. (The average symmetry in tetragonal crystals is the result of orientational disorder of $D_{2h}$-distorted fulleride anions in the tetragonal lattice formed by the cations, as shown in Fig. 2(b).) The crystal structure is mostly determined by size effects: for $A = \text{K}$ and $\text{Rb}$, $A_3C_{60}$ salts are face-centered cubic, $A_4C_{60}$ body-centered tetragonal and $A_6C_{60}$ body-centered cubic. In salts with organic cations, the symmetry can be even lower but the splitting will stay threefold as the degeneracy is completely lost already in the orthorhombic environment.

$$
\begin{array}{ccc}
D_{3d} & D_{2h} & D_{5d} \\
| & | & | \\
- & - & - \\
\end{array}
$$

Fig. 3 Symmetry lowering and crystal-field splitting of $t_{1u}$ levels in various crystallographic systems. In the case of twofold splitting, the order of levels is arbitrary. $D_{5d}$ does not occur in crystals since it is not a crystallographic point group.

Considering the abundant orbital degeneracy, the Jahn–Teller distortion is obviously another possibility for symmetry reduction. As the prerequisite for Jahn–Teller coupling is the partial filling of degenerate orbitals, it is easy to comprehend that any fulleride anion with charges different from 0 or 6 should be a candidate. Details of the Jahn-Teller effect in fullerenes have been extensively discussed in reference works. Nevertheless, we recall the main results here to emphasize the difference from inorganic systems.

In a coordination compound with a central metal ion, the Jahn–Teller distortion means that following the splitting of the degenerate orbitals of the central ion, the ligands rearrange in a different geometry of lower symmetry. If the system is a crystal, this change corresponds to a structural phase transition, since the rearrangement in one unit cell results in the rearrangement of all others to obey translational symmetry. A $C_{60}^{2−}$ molecular ion, on the other hand, can undergo a Jahn–Teller
distortion by reshaping the molecule itself, without perturbing the environment. Speaking in terms of electron–phonon coupling, the vibrations coupled to the electronic system are intramolecular in the case of fullerides, unlike the inorganic compounds, where the relevant vibrations happen between the central atom and the ligands. A striking example for this difference is that fulleride anions can show Jahn–Teller distortions in the gas phase\textsuperscript{20} or in solution.\textsuperscript{21}

In a crystal the Jahn–Teller distortion competes with the crystal field of the surrounding cations. While the crystal field induces a static distortion which can be detected by diffraction methods,\textsuperscript{22,23} the Jahn–Teller effect can induce several almost equivalent distortions along symmetry-related axes in different directions: six for $D_{5h}$ symmetry, ten for $D_{3d}$ symmetry, and twelve for $D_{2d}$ symmetry. (When the crystal field is weak, translation symmetry is not obeyed any longer by the fulleride ions and therefore $D_{5d}$ is also allowed.) If the barrier between these distortions is small, the system can move between them via pseudorotation\textsuperscript{17} if it acquires sufficient thermal energy.

The Jahn–Teller effect can only happen if the carriers are localized on the anions, i.e. they are below the Mott limit for conduction. On the other hand, the Jahn–Teller effect promotes the Mott transition by lowering the energy of the anion in the distorted state. Using the concept of such “Mott–Jahn–Teller nonmagnetic insulators”, the electronic and magnetic properties of $A_4C_{60}$ salts were successfully modeled.\textsuperscript{24,25} Jahn–Teller distortions, like other types of symmetry lowering, can be very sensitively detected by vibrational spectroscopy.\textsuperscript{26}

## 3 Optical and infrared spectroscopy in fulleride research

### 3.1 Electronic transitions

Conclusions regarding metallicity can be reliably drawn from the low-frequency optical spectra (in the far- and midinfrared). The frequency-dependent (optical) conductivity is a function which reflects charge dynamics in the solid and can be determined from measured optical quantities as transmission or reflectance, provided the measurement extends over a wide enough frequency range.\textsuperscript{27} For opaque samples as the metallic fullerides, the measurement of reflectance, evaluated by Kramers–Kronig transformation,\textsuperscript{28,29} yields the optical conductivity. Extrapolating the frequency-dependent conductivity to zero gives the dc conductivity and can be compared to transport measurements. Figure 4 shows the reflectivity curves of $C_{60}$ and the metallic fulleride $K_{3}C_{60}$. Insulators as $C_{60}$ exhibit a flat low reflectivity up to the first electronic transition (with a slight structure in the infrared due to vibrational transitions, see below), while metallic electrons cause high reflectivity in the low-frequency region (Drude absorption), followed by an abrupt decrease (the plasma edge). The optical conductivity calculated from reflectance spectra is the function directly comparable to band structure calculations.

![Fig. 4](image-url) Room-temperature reflectance spectra of $C_{60}$ and $K_{3}C_{60}$ fulleride. Note the logarithmic energy scale, 1 eV corresponds to 8065 cm$^{-1}$. The frequency extends from the far infrared through the ultraviolet. Reproduced from Ref. 10 (http://journals.aps.org/prl/abstract/10.1103/PhysRevLett.69.2284). Copyright (1992) by the American Physical Society.

### 3.2 Vibrational spectroscopy and vibronic coupling

The $C_{60}$ molecule has 174 vibrational degrees of freedom, but due to the high symmetry, only 4 of those are infrared active.\textsuperscript{6,30} These infrared-active modes in unperturbed $C_{60}$ are of $T_{1u}$ symmetry (sometimes denoted by $F_{1u}$), same as the LUMO. Thus the splitting of the vibrational modes, detected by infrared spectroscopy, mirrors the splitting of the LUMO in the anions (Fig. 3). Lowering of molecular symmetry will cause splitting of allowed modes and activation of silent modes in the infrared spectrum and is therefore a sensitive indicator of molecular distortions.

Contrary to conventional metals, vibrational transitions can be present even in the metallic state of fullerides and the details of these vibrational bands often convey important information. These weak features cannot be very well measured by reflectivity, instead the usual chemical infrared method of KBr pellets is used. Figure 5 shows the infrared transmission of a metallic and an insulating fulleride salt compared to $C_{60}$. These spectra can be recorded with very high resolution (typically well below 1 cm$^{-1}$) and fine details of the vibrational structure are detected this way. Because of the high reflectivity of most fullerides, especially towards the far in-
Infrared, the optical density derived from the transmission \((-\log T)\) does not correspond to the absorption with enough accuracy to compare it to results from theory.\(^{31}\) (This is the reason why we present our results as transmission curves in most cases.) The most important information is the frequency of the vibrational bands, the lineshape, and their change with external parameters like temperature or pressure. For the same pellet under varying conditions, a semiquantitative scaling can also be done. In practical terms, the KBr method has the advantage of preserving the composition of the samples, often arrived at by complicated synthetic pathways, and can be used under exclusion of air, as most fulleride salts are air-sensitive. KBr is transparent above 400 cm\(^{-1}\) (0.05 eV) up to the ultraviolet, therefore infrared and near-infrared spectra of the vibronic transitions and low-frequency interband transitions can be studied.

The samples have to be handled under strict exclusion of air and water, preferably in an inert gas dry box. We press our pellets under argon atmosphere and perform initial screening with a low-resolution FTIR spectrometer in an argon dry box, then fill the sample into a cryostat and do all measurements under dynamical vacuum. Reflectivity is measured in the same way, except that in this case, neat pellets\(^{28}\) or films with high surface quality\(^{10}\) are used. It is a good idea to coat the pellets with a metal layer after the measurement and use this spectrum as reference instead of a flat metal mirror, in order to correct for surface imperfections.\(^{28}\)

![Fig. 5](image-url) **Fig. 5** Infrared transmission spectra of C\(_{60}\), a metallic (K\(_3\)C\(_{60}\)), and an insulating (expanded Cs\(_3\)C\(_{60}\)) fulleride.\(^{12,33}\) The inset shows the Fano lineshape of the T\(_{1u}(4)\) mode in K\(_3\)C\(_{60}\).

Although the relationships connecting bulk reflectivity and KBr pellet transmission are too complicated for an exact description (mainly due to multiple scattering in the pellets), there are a few features in the transmission spectra indicating metallic behavior. One is the high background absorption in the infrared, corresponding to the high reflectivity, the other is the lineshape of the vibrational bands. Figure 5 shows the transmission of C\(_{60}\) and two of its salts, an insulator and a metal. Metallic K\(_3\)C\(_{60}\) shows a strong and almost featureless absorption compared to C\(_{60}\) and the insulator Cs\(_3\)C\(_{60}\). In addition, the lineshape of the highest frequency vibrational mode changes as shown in the inset of Fig. 5. The mechanism behind the lineshape is the Fano effect,\(^{34}\) the interaction of a localized excitation with a continuum. Here, the continuum is formed by the delocalized electrons and the localized mode is the molecular vibration. The mechanism is further explained for infrared spectra of organic conductors by Tanner et al.\(^{35}\)

The effect of symmetry reduction on the vibrational modes can be studied on fullerene-based polymers, where the structural changes are considerable because of the forming of intermolecular bonds.\(^{36–39}\) Figure 6 illustrates the splitting of the triply degenerate T\(_{1u}\) modes in two C\(_{60}\)-based polymers, linear RbC\(_{60}\) with D\(_{2h}\) symmetry and two-dimensional rhombohedral (C\(_{60}\))\(_n\) with D\(_{3d}\) symmetry. We observe threefold splitting for the former and twofold splitting for the latter of all modes, in accordance with group theory predictions.\(^{36}‡\) The

\(^{‡}\) Ref. 36(a) should be read together with its erratum,\(^{36}\) because of an error in

![Fig. 6](image-url) **Fig. 6** Splitting of the T\(_{1u}\) modes in the infrared spectra of C\(_{60}\)-based polymers: RbC\(_{60}\) (D\(_{2h}\)) and rh-C\(_{60}\) (D\(_{3d}\)). Reproduced from Ref. 36 (http://journals.aps.org/prb/abstract/10.1103/PhysRevB.55.10999). Copyright (1997) by the American Physical Society.
frequency of the $T_{1u}(4)$ mode, at 1429 cm$^{-1}$ in C$_{60}$, strongly depends on the charge$^{40}$ and the bonding pattern$^{41}$ and is used as a general indicator for these characteristics.

Similar, but more complicated effects are expected for the Jahn–Teller distortion in A$_4$C$_{60}$, where a competition exists between the Jahn–Teller dynamics and the tetragonal crystal field. The splitting of the $T_{1u}(3)$ and $T_{1u}(4)$ modes changes with temperature$^{42}$ (Fig. 7), while the crystal structure is preserved between 4 K and 300 K and thus there is no change in the symmetry of the crystal field.$^{15}$ At low temperature the anion assumes D$_{2h}$ symmetry, compliant with the tetragonal crystal field (Fig. 3), resulting in threefold splitting of the modes. At room temperature, a twofold splitting is apparent, which corresponds to the inherent Jahn–Teller distortion of a C$_{60}^-$ ion.$^{43}$ This Jahn–Teller distortion is dynamic, so that the average structure will remain tetragonal but the deformation is observed on the time scale of the infrared measurement. The pseudorotation in the dynamic Jahn–Teller state is made possible by the lattice expansion, and consequently, the transition temperature scales with the size of the cation in the A$_4$C$_{60}$ (A=K,Rb,Cs) series.$^{15}$ Unlike polymers, where the bond lengths change considerably, in this case diffraction studies give an upper limit of 0.04 Å for the distortion,$^{16}$ indicating the sensitivity of spectroscopy to detect molecular deformation.

Fig. 7 Splitting of the $T_{1u}(4)$ vibrational mode in the infrared spectra of K$_4$C$_{60}$ at different temperatures. Reproduced from Ref. 42 (http://journals.aps.org/prb/abstract/10.1103/PhysRevB.65.052103). Copyright (2002) by the American Physical Society.

Fig. 8 Infrared optical conductivity of K$_3$C$_{60}$ and Rb$_3$C$_{60}$. Reproduced from Ref. 29 (http://journals.aps.org/prb/abstract/10.1103/PhysRevB.51.3678). Copyright (1995) by the American Physical Society.

4 Metallic fullerides

4.1 Trivalent salts of K and Rb

The earliest measurements of IR transmission$^{44}$ or reflectance$^{40}$ were conducted on thin films starting from C$_{60}$ while in-situ doping by alkali metals and monitoring the resistivity. As these measurements had to be conducted in specially constructed cells, no other type of characterization was possible, making the assignment of stoichiometry difficult. Nevertheless, these results showed that while the resistivity decreased towards the A$_3$C$_{60}$ composition and increased subsequently up to A$_6$C$_{60}$, the overall transmission also showed an analogous pattern. Resistivity and optical data on A$_3$C$_{60}$ (where A is both K and Rb) indicated metallic character of this composition, which was further proven by reflectivity data on single-phase powders pressed into pellets.$^{28}$

Concerning the optical properties and metallicity, the papers by Iwasa et al. on A$_3$C$_{60}$$^{10,29}$ and A$_4$C$_{60}$$^{29}$ are of fundamental importance. Figure 4 shows the wide-range reflectivity of C$_{60}$ and K$_4$C$_{60}$ at room temperature. The principal difference is the low-frequency absorption by free carriers, but the vibrational features in both samples are also evident. The optical conductivity of K$_3$C$_{60}$ and Rb$_3$C$_{60}$ is compared in Fig. 8. The higher intensity of the free-carrier absorption in K$_3$C$_{60}$ indicates that it is a better metal, in accordance with its smaller lattice constant and consequently higher overlap.
Palstra et al.,\textsuperscript{45} based on the mean free path of the order of the interfullerene distance,\textsuperscript{14} gave an estimate of 500–700 (\(\Omega cm\))\textsuperscript{-1} for the limiting conductivity value for the Mott transition in \(A_3C_{60}\). Their experiments show that \(Rb_3C_{60}\) reaches this limit around room temperature, while \(K_2C_{60}\) stays in the metallic regime up to much higher temperatures. There is no saturation in the increase of the resistivity in either case,\textsuperscript{12} another sign attributed to electron correlations. A low mean free path and absence of resistivity saturation is called "bad metal" behavior and is an intriguing and not fully understood direction of condensed matter and materials physics.

The dc conductivity derived from the low-frequency extrapolation of the curves in Fig. 8 agrees remarkably well with the resistivity measurements mentioned above. Comparing the "Mott limit" estimate of Ref. 45 with the room-temperature optical conductivity data shown in Fig. 8 (Ref. 29), the extrapolated zero-frequency value for \(Rb_3C_{60}\) (355 (\(\Omega cm\))\textsuperscript{-1}) is around this limit, while that of \(K_3C_{60}\) (870 (\(\Omega cm\))\textsuperscript{-1}) is on the metallic side.

Analysis of the optical conductivity revealed that it cannot be described by a simple Drude model, instead, two Lorentz oscillators representing localized excitations had to be added (Fig. 9). Figure 9 compares the deconvolution of the optical conductivity of \(K_2C_{60}\), \(Rb_3C_{60}\) and \(K_4C_{60}\).\textsuperscript{29} The appearance of such a "midinfrared absorption" has been noted before in other "bad metal" families: cuprates\textsuperscript{47} and organic conductors.\textsuperscript{48} Here the low-frequency absorption bands can be assigned to intermolecular electron transfer, in other words hopping of localized electrons. In insulating \(K_4C_{60}\) and its analogues such excitations were observed by electron energy loss spectroscopy\textsuperscript{49} and IR transmission.\textsuperscript{15} It seems that in the conducting phases these localized excitations persist beside the free-carrier absorption.

In Fig. 10 we present transmission data in KBr pellets on trivalent alkali fullerides. The background absorption in \(Rb_3C_{60}\) increases with decreasing temperature, following the increase in the conductivity. The lineshape around the \(T_{1u}(4)\) vibrational mode depends on the cation: \(K_3C_{60}\) still shows the metallic Fano lineshape at 300 K, while in \(Rb_3C_{60}\) the low-temperature Fano lineshape starts to evolve towards a Lorentzian around room temperature. The transition from Lorentz to Fano corresponds to the Mott limit.

\subsection*{4.2 Low-dimensional polymers}

Due to its unsaturated bonds, the \(C_{60}\) molecule is prone to polymerization reactions and the subsequent formation of low-dimensional structures. The first intermolecular reaction observed was [2+2] cycloaddition. According to the Woodward-Hoffmann rules, this reaction is forbidden between two ground-state neutral molecules, but becomes allowed if one of the reactants is in a photoexcited triplet state or an anion where the \(t_{1u}\) level is populated (Fig 11). In the latter case, the resulting polymer has an unpaired electron in its \(\pi^*\) level, and because of the shortened bond length, can propagate along the polymerization axis (Fig. 12).

The phase diagram of \(AC_{60}\) (\(A=K, Rb, Cs\)) is a very rich and varied one, depending not only on temperature but also on thermal history.\textsuperscript{1,51} From structural, optical, thermal, conductivity, ESR and NMR studies and theoretical calculations, a consistent picture emerged. Three types of molecular structure appear in the phase diagram: monomeric anions, singly-bonded dimers and [2+2] cycloadduct polymers. The polymer phase forms during initial synthesis from the alkali metal and the fullerene powder; on heating, it depolymerizes into an fcc monomeric structure, consisting of separated \(C_{60}\) ions; fast cooling of this phase results in dimers at low temperature. Slow warming of this dimer phase yields first a monomeric phase around room temperature, followed by repolymeriza-
**Fig. 10** Infrared transmission spectra of K$_3$C$_{60}$ at room temperature and Rb$_3$C$_{60}$ at various temperatures$^{46}$ in the T$_{1u}(4)$ vibration region. In Rb$_3$C$_{60}$ the lineshape evolves from a Fano lineshape to a Lorentzian with increasing temperature; K$_3$C$_{60}$, which is a better metal, still shows Fano behavior at room temperature.

**Fig. 11** Energy diagram of frontier orbital interactions in [2+2] cycloaddition reactions. The reaction between two ground state molecules is forbidden according to Woodward-Hoffmann rules (a); reactions between a photoexcited and a ground state molecule (b) and between anions (c) are allowed.$^{50}$ Copyright (1994) with permission from Elsevier.

**Fig. 12** Polymerization pattern in AC$_{60}$.$^{50}$ Copyright (1994) with permission from Elsevier.

**Fig. 13** Infrared transmission spectra of C$_{60}$ and various phases of RbC$_{60}$ in KBr pellet.$^{54}$ Except for C$_{60}$, the background was not shifted along the vertical axis.

In Fig. 13, one KBr pellet is followed by infrared spectroscopy through a heat treatment sequence: starting from the polymer, the sample was heated to 425 K where depolymerization to the monomer phase occurred, then quenched to 77
K to produce the dimer phase. During the procedure, both the vibrational structure and the background change. The kinetics of the phase transitions was monitored in a more detailed way by Martin et al. on films, using the background transmission in the featureless part of the spectrum, at 900 cm\(^{-1}\). Both measurements confirm that the polymer is the most conducting phase, followed by the monomer, while the dimer phase can be regarded as an insulator. With increasing metallic background, the vibrational peaks become less prominent, but there are still distinct Lorentzian lineshapes in the monomer and polymer phase. The polymer phase is considered a correlated one-dimensional metal in this temperature range, based on ESR and microwave conductivity measurements, turning into a three-dimensional correlated metallic system with a lower conductivity upon depolymerization.\(^{56,57}\)

Over the years, several other polymeric fullerene derivatives have been prepared, many of them showing metallic character. According to quantum chemical calculations\(^{58}\) the preferred bonding pattern changes from [2+2] cycloaddition at low anionic charge (0 or 1) to single intermolecular bonds at higher charge (3 or 4). Experimental facts prove these results: \(\text{Na}_{4}\text{C}_{60}\) has a two-dimensional structure where the tetravalent anions are connected by single bonds.\(^{59}\) The spin susceptibility measured by ESR indicated a strongly correlated metal, similar to \(\text{RbC}_{60}\) or \(\text{CsC}_{60}\). \(\text{Na}_{2}\text{RbC}_{60}\) has a polymorph with a similar bonding pattern but a structure consisting of one-dimensional chains.\(^{60,61}\) ESR measurements found a Pauli-like susceptibility indicating a good metal.\(^{1}\) As in these structures the sp\(^3\) carbons prevent the formation of an aromatic system and thereby a full delocalization of electrons,\(^{58}\) it seems that electron transport can be described as of the Mott-Hubbard type rather than a band-like behavior.

### 4.3 Small cations: multiple site occupation and diffusion

In fulleride salts with cations larger than Na, the size of the trigonal aperture connecting the interstitial sites prevents the motion of the cations between these sites. For Na and smaller ions, however, interesting phenomena occur because clusters of more than one atom (not necessarily all ionized) fit into the interstitial sites, and these cations can be mobile.

The salt with the composition \(\text{Na}_{3}\text{C}_{60}\) did not fit into the series of the other alkali metal fullerenes: by electron-hole symmetry it should behave as a Mott–Jahn–Teller insulator analogous to the \(\text{A}_{3}\text{C}_{60}\) salts, yet early results showed metallic character at low temperature and an infrared spectrum typical of multiphase material at room temperature. As it turns out, homogeneous single-phase \(\text{Na}_{3}\text{C}_{60}\) only exists above 460 K, below this temperature segregated nanodomains of \(\text{C}_{60}\) and metallic \(\text{Na}_{2}\text{C}_{60}\) are formed.\(^{64}\) The separation disappears on heating by jump diffusion of the Na\(^{+}\) ions. In the high-temperature phase, the infrared spectrum corresponds exactly to a Jahn–Teller distorted \(\text{C}_{60}^{2-}\) ion, with \(D_{3d}/D_{5d}\) symmetry.

A special case of polymers is \(\text{Li}_{4}\text{C}_{60}\).\(^{65,66}\) This structure combines the [2+2] cycloaddition and single intermolecular bonding and results in a 2-dimensional network. Octahedral voids in the crystal can accommodate up to four lithium ions and the diffusion barrier is very low (about 0.2 eV). These conditions make ionic conduction possible and \(\text{Li}_{4}\text{C}_{60}\) indeed is proven to be a superionic conductor.\(^{67}\) Diffusion of lithium ions was also observed in thin films of \(\text{Li}_{4}\text{C}_{60}\) by photoemission.\(^{68}\) It is interesting that for both the bulk and thin film samples, experimental evidence points to partial charge transfer from Li to \(\text{C}_{60}\): in the films, photoemission of \(\text{C}_{60}\)\(^{68}\) and in the bulk, the shift of the Raman \(A_{g}(2)\) mode.\(^{69}\) Both estimates give around 2-2.5 electrons per \(\text{C}_{60}\). As the mobility of the lithium ions excludes possible coordination bonds between Li and the fullerene cage, it is more probable that the partial charge transfer is related to Li ion mobility and the formation of transient clusters with less than one charge per ion. The depolymerization of \(\text{Li}_{4}\text{C}_{60}\) occurs above 600 K where the charge transfer reverts to 4 (proven by Raman spectra) and metallicity is restored.\(^{69}\) The coexistence of tetravalent anions and metallicity indicates that Mott localization is absent in this material, i.e. the bandwidth is larger than the Jahn–Teller splitting. Recently, ionic conductivity has been found in \(\text{Mg}_{2}\text{C}_{60}\), a polymer isostructural to \(\text{Li}_{4}\text{C}_{60}\).\(^{70}\)
4.4 Anions with charge n > 3 and non-ionic bonding

Intercalation of C\textsubscript{60} with alkaline earth ions adds electrons to the t\textsubscript{1g} orbitals. The properties of these materials have been summarized by Iwasa and Takenobu.\textsuperscript{3} Many of them are metals, despite the low-symmetry crystal structure, with (Ba\textsubscript{6}C\textsubscript{60})\textsuperscript{71} or without (Ba\textsubscript{6}C\textsubscript{60}, Sr\textsubscript{6}C\textsubscript{60})\textsuperscript{72} a superconducting transition. Metallicity was attributed in these materials to hybridization between 5d orbitals of Ba and t\textsubscript{1g} orbitals of C\textsubscript{60}.

A special member of this family is Mg\textsubscript{5}C\textsubscript{60}, a two-dimensional conducting polymer.\textsuperscript{73} It is metallic at high temperature and turns insulating on cooling, the transition being attributed to Anderson localization on impurities. The infrared spectrum of this polymer is very different from the ones discussed so far; the highest-frequency infrared band is much higher than the T\textsubscript{1u}(4) mode of C\textsubscript{60} and it coincides with a Raman mode (Fig. 15). The Raman frequency is also upshifted from the C\textsubscript{60} A\textsubscript{g}(2) value of 1468 cm\textsuperscript{-1}, unlike Ca and Ba salts which show a downshift proportional to the nominal charge of the fulleride ion.\textsuperscript{3}

The most probable explanation for the newly appearing mode is that it is a Raman-active vibration activated by symmetry reduction due to covalent bonding to the Mg ion. A similar effect was reported for C\textsubscript{60} monolayers adsorbed on metal\textsuperscript{74} and semiconductor surfaces\textsuperscript{75} and attributed to the A\textsubscript{g}(2) mode rendered infrared active by symmetry reduction and amplified by the "vibrational phase relaxation" mechanism.\textsuperscript{76} This mechanism requires an electronic continuum and low-frequency vibrational and translational modes. The low-frequency modes are present in the polymer as the vibrations involving intermolecular bonds, and the whole effect is thus indirect proof for the presence of free electrons. The blueshift of both the infrared and Raman band is further indication for strong hybridization effects.

![Fig. 15 Infrared and Raman spectra of Mg\textsubscript{5}C\textsubscript{60}. Reproduced from Ref. 73 (http://journals.aps.org/prb/abstract/10.1103/PhysRevB.77.155431). Copyright (2008) by the American Physical Society.](image)

Infrared spectroscopy can also help in identifying bonding patterns in polymers (Fig. 16). The intermolecular single bond has a specific infrared signature around 815 cm\textsuperscript{-1}, present in all polymers containing such bonds, including single-bonded dimers. From the infrared spectra the presence of single bonds in Mg\textsubscript{5}C\textsubscript{60} could be established.

The lineshape of the vibrational bands in metallic polymers (Fig. 16) is not Fano-like, despite the delocalized character of the electrons inferred mostly from magnetic susceptibility. This behavior is probably analogous to the "bad metal" phase which develops above room temperature in Rb\textsubscript{3}C\textsubscript{60} (Fig. 10). We have observed similar changes before, in organic conductors when changing the mean free path by the introduction of defects.\textsuperscript{77} In a bad metal state, both local vibrational and electronic transitions (Fig. 9) seem to coexist with the free-carrier response.

5 Suppression of metallicity by correlations

Superconductivity of fullerenes is certainly the principal driving force behind the study of their metallic properties. We do not intend to go into the details of the superconducting state, as several excellent reviews on this subject exist.\textsuperscript{2,78} The search for new metals was driven by the possibility of increasing the superconducting transition temperature T\textsubscript{c}. The T\textsubscript{c} of early fcc alkali fullerenes showed a linear dependence on the interfullerene distance, as was expected from the BCS theory. It was believed that the best way to increase T\textsubscript{c} would be to prepare new crystals with increased lattice constant. If we take correlations into account, however, then at some interfullerene
distance Mott localization would occur and both metallicity and superconductivity disappear.

Dahlke et al. \textsuperscript{79} prepared a series of trivalent Cs-containing "extended" fulleride salts, and found $T_c$ to decrease systematically with distance. This "dome-like" dependence is typical of other families of superconductors (cuprates, heavy fermions, organic salts) where correlations play a significant role. More recently, the bottom of the dome was reached with insulating materials (NH$_3$)$_2$K$_3$C$_{60}$ and two polymorphs of Cs$_3$C$_{60}$, which however turn superconducting at slight pressure. All these observations point to these systems being on the verge of a Mott transition with the interfulleride distance controlling the parameter U/W. The exact mechanism behind the metal-insulator transition, however, is thought different in the two cases.

5.1 Loss of metallicity by reduction of symmetry

One of the first attempts to increase the lattice constant was the insertion of ammonia into the octahedral voids of K$_3$C$_{60}$ \textsuperscript{(Ref. 80)}. The crystal structure of the resulting (NH$_3$)$_2$K$_3$C$_{60}$ is orthorhombic with a very slight distortion compared to fcc K$_3$C$_{60}$, but it is an insulator. Localization of the electrons on the C$_{60}^-$ sites is further proven by antiferromagnetic order developing at 40 K.\textsuperscript{3} As other ammonia-containing fullerides with similar interfulleride distances are conducting,\textsuperscript{81} the source of the difference was suggested to be the symmetry lowering. The site symmetry of C$_{60}^-$ is C$_i$,\textsuperscript{82} causing a threefold orbital splitting shown in Fig. 3, and the observed $S=1/2$ spin state corresponds to double occupancy of the lowest lying orbital and single occupancy of the next. Dynamical mean-field theory calculations\textsuperscript{83} indeed showed that the system is so close to a Mott transition that the width of the split electronic bands is smaller than their energy difference. Pressure can drive the system across the Mott limit, resulting in a superconductor with $T_c=28$ K at 14 kbar. However, even the normal state is not without special features: the antiferromagnetic ordering below 40 K is preceded by a structural transition to an orientationally ordered phase, where the rotation of both ammonia and fulleride molecules is stopped and neighboring fulleride anions are fixed in two distinct orientations related by a 90° rotation around the c axis (Fig.2(b)), in a regular pattern. This pattern is called "ferrorotative" or "antiferrorotative", depending on the relative position of the two orientations. Rotational and magnetic order seem to be related and analogous to multiferroic behavior in inorganic systems.

5.2 Superconductors with Mott-Jahn-Teller insulating normal state

The material where fulleride anions are enclosed in the most symmetric environment found so far is the A15 extended fulleride Cs$_3$C$_{60}$, discovered in 2008 (Ref. 84). It has also the highest transition temperature ever seen in a molecular material, 38 K at 7 kbar pressure; however, at ambient pressure it is an insulator, showing antiferromagnetic ordering below 50 K. The crystal structure stays cubic throughout the whole temperature and pressure range and the anions are rotationally ordered. Magnetic measurements indicate an $S=1/2$ moment localized on the fulleride anions.\textsuperscript{85} The other polymorph of Cs$_3$C$_{60}$, with fcc structure, behaves similarly with a somewhat lower $T_c$ of 35 K and a magnetic transition below 10 K.\textsuperscript{86} which is less well characterized because of ferrorotational disorder and because the crystal structure does not permit full antiferromagnetic ordering. NMR measurements\textsuperscript{87,88} prove both polymorphs metallic in the high-pressure phase above $T_c$.

A low-spin state in a symmetric environment can only occur if there is a symmetry-breaking mechanism other than the crystal field, and the molecular Jahn–Teller effect is the obvious candidate. As the splitting of vibrational bands mimics that of the electronic ones, infrared spectroscopy is an excellent indicator of molecular distortions\textsuperscript{15,33} and can distinguish between the schemes shown in Fig. 3.

The infrared spectrum at ambient pressure is typical of an insulator at all temperatures, with a low background and Lorentzian lineshapes for the vibrational bands (Fig. 5). The Jahn–Teller effect in these materials turns out to be dynamic on a time scale comparable to that of the infrared measurement. The splitting of the infrared bands (Fig. 17) proves the symmetry lowering and shows a continuous temperature dependence which can be explained by the concept of temperature-dependent solid-state conformers applied for Jahn–Teller systems (two distorted conformers with their populations changing on heating).\textsuperscript{18}

Thus, Cs$_3$C$_{60}$ proves the Mott transition and the Jahn–Teller effect to be the driving force behind the metal-insulator transitions in fulleride salts. Intense theoretical work towards the explanation of their superconductivity complements these experimental findings.\textsuperscript{2}  

6 Conclusions

In one of the earliest review papers on alkali fullerides,\textsuperscript{7} Hadron stated: "Although the nature of the pairing mechanism in the A$_3$C$_{60}$ superconductors remains to be established, the simplicity of the materials and the progress already made suggest that a definitive resolution of this question may be achieved more quickly than in the case of the high-–$T_c$ copper oxide superconductors." The bad news is that after twenty years, the race is still on; as in the cuprates, not only the superconducting state remains unexplained, but many normal-state properties as well. The good news, however, consists of the many new experimental facts and theoretical concepts that have emerged along the way and the hope that the two problems may finally
converge into one solution.\textsuperscript{89} One should not forget the fruitful dialogue that emerged between many disciplines from condensed matter theory and quantum chemistry to sophisticated physical methods and molecular spectroscopy to explore these beautiful structures full of surprises at every step.

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