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Transition from insulating to conducting states in fulleride compounds

Ph.D. Thesis

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Chapter 1

Introduction

The discovery of the C$_{60}$ "fullerene" molecule by Curl, Kroto and Smalley in 1985 [1] opened a new era for carbon-based materials. The high symmetry of the molecule and its unusual physical properties inspired a large number of chemical studies which resulted in the synthesis of thousands of new compounds. In 1991 the synthesis of a macroscopic amount of fullerene molecules by Krätschmer et al. [2] allowed to obtain solid C$_{60}$ raising the interest of the solid state physics community.

In 1991 Haddon and coworkers [3] showed that the intercalation of C$_{60}$ crystals with alkali atoms gives rise to charge transfer fulleride salts which show metallic behavior and are superconducting with relatively high transition temperatures. In 1994 Pekker et al. found that in alkali intercalated fullerides AC$_{60}$ (A=K,Rb, Cs) the fullerene molecules are covalently bonded to each other forming one-dimensional polymeric chains. In the following years an intensive research resulted in the discovery of other one-, two- and three-dimensional polymeric structures.

The interplay of molecular and solid state properties in the fullerene molecular crystals results in a very rich physics. Fullerides are strongly correlated electronic systems in which even small differences in the crystalline structure strongly influences the ground state. Experimental evidence and theoretical calculations showed that even the Jahn-Teller effect which is difficult to observe in conventional material plays an important role in the electronic properties.

This thesis presents an experimental study of the properties of fulleride compounds obtained by electron spin resonance (ESR) and microwave conductivity measurements. The recent increase of the sensitivity and resolution of the ESR spectrometers allows to study in detail the phase distribution of these materials on a scale of some nanometers which is difficult to access by other experimental techniques. The analysis of the ESR spectrum combined with the measurements of the conductivity is a powerful method to investigate both the electronic and magnetic properties of these materials.

The first chapter is a short review of the most relevant results in the field of fullerides compounds. In the second chapter the theoretical aspects and the experimental details of microwave conductivity and electron spin resonance (ESR) measurements are presented.

The high frequency spectrometer at the Budapest University of Technol-
ogy and Economics was built between 1994-1995 by András Jánossy, Gábor Oszlányi and Titusz Fehér. The sensitivity of the spectrometer was limited mainly by the low emitted power of the source at the highest frequency (225 GHz) and by the transmission losses in the wave guides. The lack of control on the microwave power reaching the detector also limited the performance of the spectrometer.

In 2005, it was decided to modernize the spectrometer with the acquisition of a new microwave source and replacing the wave guides by a quasi-optical bridge. Previous experience on similar experimental setups at the ESR laboratory of the EPFL laboratories in Lausanne suggested the importance to isolate the spectrometer vibrationally from the ground. Relative displacements between the magnet and the optical bridge results, in fact, in a change of the optical path which induces a noise at the detector. For these reasons, we placed the spectrometer on a vibration-isolated supporting structure. I participate to the design of the structure in collaboration with Dr. Reis of the Building Acoustic Laboratory and Dr. Kiss and Dr. Hunyadi of the Structural Department. The structure consists of a 2-ton concrete mass isolated from the ground by 36 copolymeric blocks and 4 brick columns strengthened by aluminum shafts supporting the optical table. Ferromagnetic materials which could influence the homogeneity of the magnet were avoided. The self resonant frequency of the structure is only 10 Hz. Mechanical vibrations with higher frequency are damped efficiently. The design of the new elements of the spectrometer was completed in the summer of 2006. The construction of the supporting structure begins in September and ended in March 2007. The the first spectrum was collected in April 2007.

One of the first problem that I studied during my Ph.D. was the nature of the ground state of the Na$_2$C$_{60}$ fulleride. This fulleride was believed to be an insulator due to the cooperative influence of the Jahn-Teller effect and electron-electron correlations. High frequency ESR measurements performed by me in 2005 and presented in chapter 4 contributed to show that the electronic properties of this fulleride are instead determined by a segregation of the Na$^+$ ions in domains with different concentrations. This study was made in collaboration with the groups guided by Katalin Kamáras and Sándor Pekker of the Research Institute of Solid State Physics and Optics (SZFKI) of the Hungarian Academy of Science.

The collaboration with the SZFKI group continued in the following three years with the study of two fulleride polymers characterized by a structural disorder which strongly influences their electronic and magnetic properties. On the bases of ESR and microwave conductivity measurements, presented in chapter 5 we suggested that these two polymers are metallic and go through an Anderson localization of the electronic states with lowering temperatures.

Chapter 5 presents a study of the transport properties of the Li$_4$C$_{60}$ fulleride polymer made in collaboration with the group of Mauro Riccò of the University of Parma (IT) and Gábor Csányi of the University of Cambridge (UK). Frequency dependent conductivity and nuclear magnetic resonance measurements combined with theoretical calculations showed that this polymer is an ionic conductor due to the diffusion of the Li$^+$ ions. High frequency
ESR measurements performed by the new spectrometer combined with a study of the microwave conductivity showed a contribution to the conductivity given by the hopping of localized electronic states attributed to small polarons.
Chapter 2

Fullerene Solids

2.1 Introduction

Fullerene solids are molecular crystals in which the interplay of the molecular and solid state properties results in a very rich physics. In this chapter, we present a brief review of the structural and magnetic properties of fullerene solids.

Due to the vast amount of experimental results and theoretical calculations reported in the last 20 years on these materials it is not possible to give here a complete account of the field. Only the aspects relevant to the thesis are presented. Particular attention will be given to the materials which are obtained by intercalation of fullerene crystals with alkali and alkali-earth atoms. More complete reviews are given by Dresselhaus [4] and Forró and Mihály [5]. Many aspects of the electronic properties of fullerene solids, with particular attention to superconductivity, are treated by Gunnarsson [6, 7].

2.2 The C\textsubscript{60} molecule

The C\textsubscript{60} "fullerene" molecule was discovered by Curl, Kroto and Smalley [1] in 1985 and became rapidly the object of study of many research groups due to its highly symmetric shape and unusual electronic properties. The C\textsubscript{60} molecule is formed by 60 carbon atoms positioned at the vertices of a truncated icosahedron (Fig. 2.1). This structure belongs to the highest symmetry point group, \textit{Ih}, and is formed by 20 hexagonal and 12 pentagonal carbon rings. The diameter of the molecule is 7 Å with a 4 Å cavity inside.

The curved surface strongly modifies the hybridization of the 2s and 2p electron orbitals of the C atoms which have both \textit{sp\textsuperscript{2}} and \textit{sp\textsuperscript{3}} character. Each carbon is equivalent and connected to the three nearest neighbor atom by distorted \textit{sp\textsuperscript{2}} bonds and has an occupied \pi orbital directed normal to the surface of the molecule. The \pi orbitals are distorted by the curved cage of the molecule in a way that the electrons spend more time outside the fullerene than inside. This effect enhances the overlap between the orbitals of nearest neighbor C\textsubscript{60} molecules in the fulleride crystals influencing their band structure.

Contrary to graphite, the \pi orbitals are not delocalized on each C-C
bonds. The edges shared by two hexagons have a double bond nature and are 1.391 Å long while the single bonds at the edge of the pentagons are somewhat longer (1.455 Å). The pentagonal carbon rings are responsible for the high electron affinity of the molecule which is estimated to be about 2.65 eV.

The electronic configuration of the fullerene molecule can be computed with a simplified LCAO method based on symmetry considerations according to Hückel [4, 8]. This model computes the energy levels for the 240 valence electrons of the carbons considering all the 60 atoms equivalent. Of these 240 electrons 180 are in the localized $\sigma$ molecular orbitals with energies that lie well below (a few eV) the Fermi energy. The transport and the optical properties of the fullerenes depend on the configuration of the remaining 60
electrons. In Fig. 2.2 the energy level diagram of the C_{60} molecule labeled according to the irreducible representation of the I_h point group is shown [8]. The electronic configuration is characterized by a full HOMO level and an empty LUMO level with an energy gap of 1.92 eV.

2.3 Crystalline compounds

2.3.1 Crystalline C_{60}

In 1991 the synthesis of a macroscopic amount of fullerene molecules allowed the study of solid C_{60} [2]. The C_{60} molecules form a close packed cubic molecular crystal called fullerite which is stable up to 700 K at ambient pressure. The crystal undergoes a first order phase transition at 261 K from a high temperature phase in which the C_{60} molecules are almost freely rotating to an orientationally ordered low temperature phase.

For $T > 261$ K, the crystal lattice is fcc with a lattice parameter of 14.17 Å (Fig. 2.3). In this phase, as in other van-der-Waals solids constituted of round shape molecules (e.g. benzene), the fullerene molecules rotate almost freely with a period of about $10^{-11}$ seconds. The molecules assume a spherical symmetry due to the rotation. For this reason the resulting structures belongs to the Fm3m space group although the C_{60} molecule has no four-fold axes.

When the temperature is lowered below 261 K, the reciprocal orientations of the molecules start to be correlated and the rotation becomes constrained to specific axes [4]. The molecules jump between four different possible orientations changing the rotation axes at discrete time intervals. The four orientations are obtained by rotating the molecule around the local (111) axes of 22 – 26° with respect to the standard orientations shown in Fig 2.3. The standard orientations are those which maintain the highest symmetry ($T_h$) compatible with the fcc lattice and the icosahedral shape of the molecule. The resulting structure has four fullerene molecules per unit cell and belongs to the Pa3 space group. With this reciprocal orientation, the molecules face the electron-rich double bond against the electron-poor pentagon of their neighbors minimizing the repulsion forces.

At about 90 K, a second order phase transition takes place when jumps between the different orientations freeze. The resulting structure is characterized by a "merohedral" disorder in the relative orientations between the C_{60}'s.

2.3.2 Alkali intercalated fulleride salts

The fullerite structure described in Sec. 2.3.1 has three interstitial sites. One has octahedral symmetry and two smaller ones are tetrahedral. Due to the large, (10 Å), center to center distance between two neighboring C_{60}'s, the interstitial sites can contain even large atoms or small molecules. A charge transfer between the intercalated atoms and the strongly electron acceptor fullerene molecules takes place, giving rise to charge-transfer salts or poly-
Figure 2.3: Left: Illustration of the C_{60} crystal. Right: Schematic representation of the two possible orientations of the C_{60} molecule in the cubic lattice [5].

...meric structures that will be described in the following section. The charge transfer is complete in most alkali intercalated salts with the exception of Na_{10}C_{60} and Li_{1}C_{60} compounds. Partial charge transfer was also observed in alkali earth intercalated salts.

The crystal structure and the dynamics of the C_{60} molecule of fulleride salts are strongly influenced by the size of the intercalated atoms. The dimension of the interstitial sites depends on the relative orientation of the C_{60}'s and large atoms can be accommodated in the fullerene crystal only if the molecules assume a given orientation. An analysis of the orientation dependent potential which determines the arrangement of the molecules in alkali fulleride salts was given by Yildirim et al. [9]. For small intercalated atoms, the orientation of the fullerene molecules is the result of the interplay of the cation-C_{60} and C_{60}-C_{60} interactions. Both of these interactions are minimized by the orientation in which a double bond faces to a tetrahedral cation. This results in an orientationally ordered Pa\overline{3} phase as in pure fullerite in which the molecular rotation is hindered even above room temperature.

In the case of large cations (K^+, Rb^+ and Cs^+) the strong repulsive interaction due to the short cation-anion distances is predominant and stabilizes a structure in which the fullerenes assume one of the standard orientations facing the hexagon to the cation. Even in these structures, the molecular rotation is strongly constrained.

The lattice of A_{x}C_{60} (A=K, Rb and Cs) fullerite remains fcc in the case of single interstitial sites occupancy, i.e. for x ≤ 3, while it is distorted for higher occupancy. In the case of smaller ions, like Na^+, the fcc lattice is compatible with multiple site occupation.

In AC_{60} (A=K, Rb and Cs), the phase stable at high temperature (T > 450 K) has a rocksalt structure in which the A ions occupy the octahedral site of the fcc fullerene lattice without significantly influencing the rotation of the molecules. The low temperature phases are polymer compounds that will be presented in Sec 2.3.4.

In A_{3}C_{60} (A = K and Rb), the strong short-range repulsive interaction be-
tween the large A ions in the tetrahedral sites and the C_{60} molecules forces the fullerene molecules to assume one of the two standard orientations which makes the tetrahedral sites larger. This interaction stabilizes a Fm\overline{3}m structure. Although the lattice has four-fold rotation axes, the molecules are not rotating due to the merohedral disorder which arises from the random occupation of the standard orientations [10]. In Cs_{3}C_{60}, the Cs\textsuperscript{+} anions are too large to enter the tetrahedral sites and this results in a multiphase structure which is a mixture of body-centered orthorhombic (bco) and A15 phases. A single-phase bco material forms applying pressures higher than 20 kbar [11].

The fcc lattice distorts to body centered tetragonal in A_{4}C_{60} (Ar,K and Rb) to allow the insertion of two ions in the octahedral site [12].

In A_{6}C_{60} all molecules have the same relative orientation. The tetrahedral sites of this structures are all equivalent. They are surrounded by two pentagons and two hexagons. All molecular rotation is hindered and only librations around the equilibrium positions are allowed.

Fulleride salts intercalated with Na are the subject of Chap. 4. Here we mention only that the small Na\textsuperscript{+} ions can form cubic intercalated salts even with high concentrations as in Na_{9}C_{60}. The fulleride salt with the highest Na content per unit cell synthesized up to now is Na_{10}C_{60} [13]. In this compound the C_{60}\textsuperscript{6−} are observed with n = 8 instead of the expected total charge transfer n = 10. This was explained by the formation of Na\textsuperscript{+} ion clusters inside the octahedral site [13].

The study of the Li-C_{60} phase diagram is complicated by the small size of the Li atom which allows multiple occupations of the interstitial sites and it also gives rise to diffusion. This results in multiphase materials with poorly defined structures. Synthesis of Li_{x}C_{60} compounds with Li contents x = 1–30 are reported [14, 15]. For x > 7 Li atoms form clusters which increase the interfullerene distance and reduce the charge transfer between the C_{60}'s and the Li atoms. To our knowledge, only Li_{16}C_{60} was reported to be single-phased and monomeric [14].

### 2.3.3 Alkali-earth intercalated fulleride salts

Very few studies were reported on alkali-earth intercalated fullerenes relative to those published on alkali fullerides probably due to the difficulties in the synthesis of single-phase samples.

Ca was reported to form solid state solutions with C_{60} with a Ca content up to five. Ca_{5}C_{60} was reported to have a cubic (Pa\overline{3}) structure [16]. A scanning tunnelling microscopy study indicated the formation of four-membered clusters in the octahedral site and the occupation of one tetrahedral site by the fifth Ca\textsuperscript{2+} cations [17].

Ba and Sr intercalated fullerenes are believed to have an incomplete charge transfer and strong hybridization between the electrons of the alkali earth atom and the fullerene molecule [18, 19]. Ba_{3}C_{60} was reported to have an interesting sc A15 structure in which the C_{60}'s take perfectly alternately one of the two possible standard orientations suppressing the merohedral disorder that characterize the A_{3}C_{60} alkali intercalated salts [20]. Synthesis of orthorhombic Ba_{4}C_{60} and body centered cubic Ba_{6}C_{60} multiphase samples
was reported by Baenitz and Brown [18, 19]. The existence of single-phase 
\textit{boc} \ Ba_x C_{60} \ was \ also \ reported \ [20, 21]. \ To \ our \ knowledge, \ two \ phases \ were 
recognized \ in \ the \ Sr_x C_{60} \ phase \ diagram \ with \ \( x = 4 \) \ and \ \( x = 6 \).

\subsection{2.3.4 Fulleride polymers}

In 1993 Rao and coworkers made the remarkable discovery that fullerene 
molecules can form covalent bonds between each other through a \((2 + 2)\) cy-
cloaddition reaction, when exposed to ultraviolet light, in absence of oxygen 
\[22\]. This results in a one-dimensional polymeric chains in which the fullerene 
molecules are bonded by four membered carbon rings as shown in Fig. 2.4. 
The covalent bonds distort the molecules which become elongated along the 
direction of polymerization and shrinks the interfullerene distance from 10 
to 9.1 Å.

![Figure 2.4: Crystal structure of the fulleride photopolymer [23].](image)

The conditions under which covalent bonds form through a \((2 + 2)\) cy-
cloaddition reaction can be understood considering the molecular orbitals of 
two neutral fullerene molecules shown in Fig. 2.5. When the high energy 
molecular orbitals \( t_{1u} \) is unoccupied the formation of the covalent bond re-
quires a great activation energy. If instead, the \( t_{1u} \) level is populated bonding 
is favorable [23]. Electrons can be promoted to the \( t_{1u} \) level by absorption of 
light as in the case of photopolymers or by charge transfer from donor atoms 
as in intercalated salts. Quantum chemical calculations [24] confirmed that 
\( C_{60}^{n^-} \) anions are unstable to the formation of \((2 + 2)\) cycloadducted covalent 
bonds for low values of \( n \) while for \( n \geq 3 \) the single-bond configurations are 
more stable.

Polymerization of \( C_{60} \) molecules was induced by applying pressures of 
a few GPa also [26] (see Fig 2.8) . The first alkali intercalated fulleride 
photopolymer was discovered in 1994 when Pekker and coworkers recognized that 
the orthorhombic phase of \( AC_{60} \) (K, Rb, Cs) is a one-dimensional fulleride 
polymer [27, 28]. In this case, polymerization takes place spontaneously 
and reversibly between the \( C_{60}^{n^-} \) anions. This is in contrast with photo-
and pressure polymerization which is irreversible. \( Na_2AC_{60} \) (A=K, Rb) is a 
linear polymer in which the fullerene molecules are single-bonded as shown 
in Fig. 2.6 [29]. Single-bond configuration were found also in the \( Na_4C_{60} \) 
two-dimensional polymer [30] confirming the theoretical calculations.

Although it is energetically favorable, polymerization is observed quite 
rarely. The four membered carbon rings form only if the two fullerene 
molecules face double bonds to each other. This orientation is not ener-
getically favorable because it brings two electron rich parts of the molecules 
close to each other. For this reason \((2 + 2)\) cycloaddition takes place only
Figure 2.5: Molecular orbital energies of two reacting fullerene molecules when an electron is promoted by absorption of a UV photon in the $t_{1u}$ levels (left) or by charge transfer from an intercalated atom (right) [25].

when fullerenes rotate almost freely. This explains why, e.g., $A_3C_{60}$ fullerides do not polymerize.

Lattice expansion due to large counter-ions can inhibit polymerization. This is the case of the linear $Na_2AC_{60} \ (A=K, \ Rb, \ Cs)$ polymers. The K intercalated compound polymerizes completely while in $Na_2RbC_{60}$ it takes place only partially giving rise to an inhomogeneous material [29]. A moderate pressure of 0.9 GPa is needed to stabilize the polymerization in $Na_2CsC_{60}$ [29]. The same mechanism is observed in the Li-$C_{60}$ system. For low intercalation levels, polymeric structures form. LiC$_{60}$ was reported to be a two-dimensional (2+2) cycloadducted polymer [31] but this result was not confirmed by other groups. Li$_4$C$_{60}$ has an unusual two-dimensional polymeric structure in which double and single interfullerene bonds coexist (see Fig. 2.7) [32]. For higher intercalation levels, the formation of Li clusters reduces the efficiency of the charge transfer and increases the interfullerene distance thus preventing polymerization.

Figure 2.6: The "single-bond" structure of the $Na_2AC_{60} \ (A=K, \ Rb, \ Cs)$ linear polymers [5].

The formation of single bonded configurations is less limited by geometric constraints. A dimer phase of $AC_{60} \ (K$ and Rb) formed after quenching below 270 K, where the molecular rotation is hindered [33].
2.3.5 Cubane-fullerene cocrystals

The large dimension of the interstitial sites of the fullerite structure allows to intercalate small molecules as well. One of the most interesting examples is the intercalation of NH$_3$ molecules in the structure of Na$_2$CsC$_{60}$ [34].

Recently Pekker et al. intercalated cubane (C$_8$H$_8$) molecules in the octahedral site of the C$_{60}$ and C$_{70}$ crystals [35]. The cubane molecule consists of 8 carbon atoms sitting at the vertexes of a regular cube and 8 C-H bonds directed outwards along the body diagonal. The structure of the cubane-fullerene cocrystal is shown in Fig 2.9. The two molecules do not react with each other at temperatures lower than 400 K and form an fcc structure in which the interfullerene distance is increased from 10 to 10.42 Å. Surprisingly, the rotation of the fullerenes is favored by the insertion of the cubane molecules in contrast to the intercalation of atoms. The temperature at which the rotation becomes hindered lowers from 261 K in pure fullerite to 140 K in the cocrystal phase. The increased lattice constant which weakens the repulsive interaction between the C$_{60}$ and the perfect match between the concave surface of the fullerene and the convex surface of the cubane molecule lowers the onset temperature of rotation.

The fullerene-cubane cocrystals show an interesting behavior also at high temperatures. For $T > 470$ K, the cubane molecules isomerize into a more stable configuration. This induces a solid state reaction with the fullerene molecules and a copolymer forms. The structure of the copolymer is only partially known.

2.4 Phonon spectrum

The molecular nature of the fullerides is reflected in the phonon structure as shown in Fig. 2.10. Due to the weak interaction between the fullerene molecules, intra-molecular and inter-molecular vibration modes can be distinguished. The intra-molecular modes cover the range of frequencies be-
tween 200 cm\(^{-1}\) to 2000 cm\(^{-1}\). At lower frequencies (50-100 cm\(^{-1}\)) modes that involve a relative motion between the C\(_{60}\) and the intercalated atom are found. The interfullerene phonon frequencies are in the range of some tenths of cm\(^{-1}\) due to the high mass of the fullerene molecule. At the lowest frequencies (about 10 cm\(^{-1}\)) the remaining molecular dynamics is due to small angle rotations around the equilibrium positions called librations.

2.5 Electronic properties

One of the most interesting aspects of the physics of fulleride compounds is the interplay between the molecular and the crystalline nature that characterize their physical properties.

The description of the electronic properties of fullerides can be made in the framework of the Hubbard model. This model describes the insulating or conducting nature of the electronic states in a solid as the result of the balance of two energy terms. The first energy term is the gain due to the hopping of the electrons between the lattice sites (the fullerene molecules in this case). Its magnitude is estimated to be of the order of the band width \(W\).
The second term is described by a parameter $U$ which represents the energy cost of a doubly occupied site, i.e., in fullerenes, of a molecule, due to the Coulomb repulsion of the electrons. Electron hopping is not energetically favored if the Hubbard $U$ is large. A material with an integer number of electrons per site is expected to be an insulator if the ratio $U/W$ is larger than one.

As we discussed in Sec. 2.2, the radiating $\pi$ orbitals of the carbon atoms point prevalently outside the molecules giving rise to electronic bands in the crystalline phase. The bands that play a role in the electronic properties of the fullerenes originate from the energy levels: $h_u$, $t_{1u}$ and $t_{1g}$. Pure fullerite is a band insulator with a full five-fold degenerate $h_u$ band and an empty $t_{1u}$ conduction band. The electrons transferred from the intercalated atoms occupy the $t_{1u}$ and $t_{1g}$ bands. The band-width, $W$, is only of the order of 0.5 eV due to the limited overlap of the orbitals, while the Hubbard $U$ is about 1 eV.

According to this model, fullerenes compounds should be insulating. Interestingly, it was found instead that while $A_4C_{60}$ is insulating $A_3C_{60}$ is metallic down to 19 K where it becomes a superconductor. Theoretical explanations for these differences were reported and will be summarized in the following.

Electron-electron correlations are important in determining the electronic behavior of alkali intercalated fulleride polymers. In the case of $AC_{60}$ linear polymers, the reduction of dimensionality due the formation of the $C_{60}$ chains has to be taken into account also to describe their ground state.

### 2.5.1 Metallic behavior of $A_3C_{60}$ ($A=K$, Rb)

These fulleride salts have a half filled degenerate conduction band with a large $U/W$ ratio, $U/W = 1.5 - 2.5$. A metal-insulator transition is predicted to take place for $U/W = 1.5$ by a simple Hubbard model.
The metallic behavior of $A_3C_{60}$ was explained as a consequence of the triple degeneracy of the conduction band by Gunnarsson [6, 7]. According to the calculations the inclusion of the degeneracy of the band, $N_d$ in the Hubbard model raises the critical value $(U/W)_c$ ratio from 1.5 to $1.5 \cdot \sqrt{N_d}$. For a three fold degeneracy the critical value is $(U/W)_c = 2.6$. According to this interpretation, the high symmetry of the molecule and the Fm$3$m cubic lattice of the $A_3C_{60}$'s drives these fullerides to be metallic down to the superconducting transition temperature ($T_c = 19.3$ K for K$_3$C$_{60}$) [3].

**2.5.2 The Jahn-Teller-Mott insulating ground state**

$A_4C_{60}$ fullerides are insulators, in spite of the partially filled $t_{1u}$ band. The difference between the ground states of $A_3C_{60}$ and $A_4C_{60}$ was ascribed by Fabrizio and Tosatti to a Jahn-Teller distortion of the fullerene molecules [37, 38]. In the following, we briefly summarize the main concepts of the theory.

The Jahn-Teller theorem states that non-linear molecules with partially filled degenerate HOMO orbitals distort the configuration in order to lift the degeneracy. The electrons occupy the lower energy level compensating for the gain in energy associated to the deformation, lowering the total energy of the molecule.

This effect is expected to be important in fullerenes due to the high degeneracy of the electronic levels and large electron-phonon coupling. In the case of an insulating $C_{60}$ compound the computation of the Jahn-Teller distortion requires to solve the problem of the interaction of a triply degenerate electronic level with a fivefold degenerate phonon mode [38]. The splitting for different electron fillings of the level is shown in Fig. 2.11.

The gain due the JT effect is larger for even filling-numbers than odd ones. Usually this effect is much smaller than the band-width and does not play any role in determining the ground state. As seen in Sec.2.5, fullerides
Figure 2.11: Splitting of the $t_{1u}$ electronic level as a function of the filling-number. Note the higher energy gain for even number of electrons [38].

have a particularly narrow band and even small energy contributions can drive them through a metal-insulator transition. It has been showed that the JT effect results in a modulation of about 100 meV of the Hubbard $U$ [39]. As a consequence of this modulation, the Hubbard $U$ is larger for fullerenes with an even filling level, as for $A_4C_{60}$, inducing a transition to an insulating ground state. The opposite is realized in compounds with odd number of electrons per molecules explaining the metallic state of the $A_3C_{60}$ fullerenes.

### 2.5.3 Alkali-earth salts

Metallic behavior was observed in fullerene thin films intercalated with Ba and Sr while Mg intercalation resulted in semiconducting behavior [40].

Superconductivity was observed in alkali-earth intercalated fullerenes for the first time by Kortan and coworkers in 1992 who found that the $Ca_6C_{60}$ salt is superconducting with $T_c = 8.4 \, K$ [16].

Afterwards, many groups looked for superconductivity in Ca, Sr, Ba intercalated fullerenes but the results were controversial. $Sr_xC_{60}$ with $x = 4, 6$ were claimed to have a critical temperature of about 4.4 K by Kortan’s group [41] while metallic behavior was observed by Gogia et al. [21]. Superconductivity was observed in $Ba_6C_{60}$ by Kortan et al. [42] while Baenitz et al. [19] indicated $Ba_4C_{60}$ as the superconducting phase.

### 2.5.4 Dimensionality of the electronic states in $AC_{60}$ polymers ($A=K, Rb, Cs$)

The presence of the linear polymeric chains suggested that the anisotropy of the structure is reflected also in their electronic configuration.

The $AC_{60}$ ($K,Rb$ and $Cs$) polymers are strongly correlated metals at room temperature as demonstrated by the large spin susceptibility (see Sec. 3.3.2) [43, 44]. The distortion of the molecules in the direction of the polymeric chains lifts the degeneracy of the $t_{1u}$ conduction band so the band filling is not $1/6$ but $1/2$. Half filling of the band and the strong electron-electron correlation both favor electron instabilities.
Figure 2.12: Different relative orientations of the polymeric chains in KC$_{60}$ (left) and RbC$_{60}$ (right) after [45]. The polymeric chain is directed along the $a$ crystallographic direction. The shaded bars represent the plane of the four-membered carbon ring bonding the molecules projected on the $bc$ plane.

ESR and conductivity measurements showed that KC$_{60}$ is metallic down to the lowest temperatures while RbC$_{60}$ and CsC$_{60}$ undergo through a phase transition to a spin density wave ground states at about 50 K [44, 46]. To explain the different ground state it was suggested that KC$_{60}$ is a three dimensional anisotropic metal while the Rb and Cs intercalated polymers have a quasi one-dimensional electronic band structure.

Although a direct measurement of the anisotropic conductivity was not yet reported, this scenario can be considered plausible on the basis of NMR and ESR measurements and on the single crystal X-ray diffraction data by Launois et al. [45]. The authors observed a difference in the relative orientation of the polymeric chains in the polymers as shown in Fig. 2.12. This difference can influence the inter-chain orbital overlap and the dimensionality of the electronic states.

The high temperature monomeric phases of AC$_{60}$ are insulators with a small gap. This was interpreted as a consequence of a smaller overlap between the $\pi$ orbitals due to the increased inter-fullerene distance and molecular rotation.
Chapter 3

Experimental methods

3.1 Introduction

In this chapter the basic concepts of microwave conductivity and electron spin resonance (ESR) measurements will be presented. The combined use of these two experimental techniques is of great help in understanding the phase distribution, the electronic and magnetic properties of samples with rich phase diagrams such as fullerides.

High frequency ESR spectra at 75, 111.2, 222.4, 225 GHz presented in the following chapters were measured at the ESR Laboratory of the Budapest University of Technology and Economics. During my stay at the laboratory, I also took part in the development of the spectrometer. This consisted of replacing the conventional wave-guide based transmission setup by a new quasi-optical bridge and the construction of a vibration damping supporting structure and a new probe head. Most of the measurements presented in the following chapters were carried out with the old spectrometer so both experimental setups will be presented. To provide an overall picture, the most important technical aspects of the commercial spectrometer (Bruker Elexsys E500) used for the 9 GHz ESR measurements will also be described.

At the end of the chapter, the other experimental techniques used in addition, such as SQUID magnetometry, infrared and Raman spectroscopy will be discussed also.

3.2 Microwave conductivity measurements

3.2.1 Basic concepts

The cavity perturbation technique allows to measure the conductivity of a sample in the GHz frequency range without contacting it. The absence of electric contacts in conductivity measurements is a great advantage for porous and air sensitive samples, usually sealed in a quartz tube under inert atmosphere. Conductivity of pellets prepared by pressing powder samples can be dominated by the inter-grain percolation conductivity which is not intrinsic to the material. Modification of the crystal structure in pellet samples by the applied pressure or creation of Schottky barriers at the contacts
can also affect the measured value of the conductivity.

The basic ideas of the cavity perturbation method were developed in the 60-ies -70-ies [47, 48, 49] and with the development of the technical instruments many variations were presented [50]. The conductivity of the sample is obtained from the changes in the quality factor, \( Q \), and the resonance frequency of a microwave resonant cavity (resonator) due to the insertion of the sample. A microwave cavity is a metallic box which sustains electromagnetic standing waves. It has usually a cylindrical or rectangular shape and characteristic dimensions comparable to the microwave wavelength.

Due to the high conductivity of the walls, microwave radiation coupled in the cavity is multiply reflected with low losses. Standing waves (called modes) store the microwave energy inside the cavity. Near a resonance, the power absorption spectrum of the cavity is a Lorentzian:

\[
P(\omega) = \frac{1}{4(\omega - \omega_0)^2 + (2\pi \Gamma)^2},
\]

where \( f_0 = \omega_0/(2\pi) \) is the resonance frequency of the mode, \( \Gamma \) is the width of the absorption. We define the quality factor, \( Q \), by:

\[
Q = \frac{\langle W \rangle}{L},
\]

where \( \langle W \rangle \) is the time-averaged microwave energy stored in the cavity and \( L \) is the energy loss per cycle. Typical values of \( Q \) are \( 10^3 - 10^6 \) for microwave cavities made of metallic and superconducting materials, respectively. It can be shown that this definition is equivalent to the more practical expression:

\[
Q = \frac{f_0}{\Gamma}.
\]

The quality factor is determined experimentally from the center frequency and the width of the power absorption of the cavity.

Microwaves induce eddy currents in a sample inserted in the cavity which changes the resonance frequency and lower the quality factor. The different contributions to the overall losses \( L \) in the cavity can be separated as \( L = L_{\text{cavity}} + L_{\text{sample}} \). Substituting this expression in eq. 3.2 the quality factor can be expressed as the sum of two terms:

\[
\frac{1}{Q} = \frac{1}{Q_{\text{cavity}}} + \frac{1}{Q_{\text{sample}}},
\]

The values of \( Q \) and \( Q_{\text{cavity}} \) can be measured separately by measuring the quality factor of the cavity with and without the sample.

Detailed calculations of the relations between the real and and imaginary part of the conductivity, \( \sigma_1 \) and \( \sigma_2 \), and the \( Q \)-factor and frequency shift in the cavity in a wide range of different sample geometries can be found in the literature [50]. Here we report the results for a spherical sample.

In Fig. 3.1 the loss \( \Delta(1/Q) \) induced in a TE001 cavity by a spherical grain of diameter \( a \) as a function of the conductivity \( \sigma \) is shown [51]. In a TE011 cavity the sample can be positioned in an antinode of the magnetic or of the electric field. The losses are maximized if the sample is in the
maximum of the electric field $E_\omega$ when the conductivity of the sample is low and in a maximum of the magnetic field $H_\omega$ for higher values of $\sigma$. In conducting samples ($H_\omega$ curve) we find two regimes. The first one is called depolarization regime, for values of $\sigma$ below the maximum of the curve, when the grain size $a$ is smaller than the penetration depth and the losses increase with increasing conductivity. The second one, the skin-depth regime, for higher values of $\sigma$ when the microwave can only partially penetrate in the sample and losses decrease with increasing conductivity.

Metallic fulleride powders have a conductivity of about $10^3 \ \Omega^{-1}\text{cm}^{-1}$ [6, 7] and typical grain size $a$ equal to 10-100 $\mu m$ so the best geometry for microwave conductivity measurements is the maximum of the magnetic field.

### 3.2.2 Microwave conductivity measurements in powder samples

In low conductivity powder materials the typical grain size is much smaller than the penetration depth and the magnetic field has an approximately constant value inside the grain. A simple estimation of the dissipated power for a sample in the maximum of the magnetic field can be done computing the ohmic losses in the individual grains considered as spheres and neglecting percolation currents between them.

In this configuration, the eddy currents are driven by the electric field $E_\phi$ tangent to the surface of the sphere which is induced by the oscillating magnetic field $\vec{B}(t)$ according to the Maxwell equation $\nabla \times (\vec{E}) = -\partial \vec{B}/\partial t$, as shown in Fig. 3.2.

The microwave ohmic losses $L_{\text{grain}}$ due to the current density $\vec{J} = \sigma \vec{E}$ in a sample with conductivity $\sigma$ is:

$$L_{\text{grain}} = \left\langle \int \vec{J} \cdot \vec{E}_\phi dV \right\rangle = \frac{\pi B_0^2 \sigma R_5^5}{5}$$ (3.5)
Where \( R \) is the radius of the sphere and \( B_0 \) is the amplitude of the magnetic field at the position of the grain. The overall dissipated energy per second is \( N \cdot L_{\text{grain}} \) where \( N \) is the number of grains in the sample. This result combined with Eq. (3.2) gives an inverse proportionality relation between \( Q_{\text{sample}} \) and \( \sigma \). However, the proportionality constant cannot be determined precisely for powder samples because the distribution of the grain radius \( R \) is unknown. Percolation currents at the edges of different grains can also give contributions that are very difficult to estimate. For these reasons the absolute value of the conductivity cannot be measured for powder samples. The metallic/insulating nature of the sample or electronic or structural phase transitions can be detected, however, from the temperature dependence of the \( Q \) factor.

![Schematic view of the eddy currents induced by the time dependent magnetic field \( B(t) \) in a spherical grain.](image)

Figure 3.2: Schematic view of the eddy currents induced by the time dependent magnetic field \( B(t) \) in a spherical grain.

With a more general treatment [50, 51], it is possible to show that the frequency shift for a sample in a node of the electric field is only slightly dependent of the conductivity in the depolarization regime thus it is not as informative as the \( Q \) factor.

### 3.2.3 Experimental setup

The sample sealed in a quartz tube is positioned at the center of a cylindrical copper cavity operating at about 10 GHz in the TE001 mode. This position is a node for the electric field and a maximum for the magnetic field. The electrical and magnetic field distribution inside the cavity is shown in Fig. 3.3. During the measurements, the microwave cavity is kept at constant temperature by thermalization with flowing water. A double-wall gas-flow quartz cryostat inserted axially in the cavity from the top allows to change the temperature of the sample between 130 and 700 K.

As described in the Sec. 3.2.1, the frequency response of the cavity is a Lorentzian line centered at the resonance frequency of the cavity. In theory, the \( Q \) factor can be obtained by eq. (3.3) sweeping the frequency of the
microwave radiation coupled into the cavity and measuring the Lorentzian power absorption spectrum. This approach is quite slow because it requires to fit a Lorentzian to extract the parameters. For this reason the frequency sweep method is used only to determine the resonance frequency at the beginning of the measurements. The temperature dependent measurements are instead performed following an ac method developed by Mehring and coworkers [52]. This technique allows fast measurements of the Q factor with a relatively simple experimental apparatus. The basic idea is to modulate the frequency of the microwave radiation with amplitude Ω and frequency \( \omega_m \) around the resonance frequency \( \omega_0 \): \( \omega(t) = \omega_0 + \Omega \sin(\omega_m t) \). The power spectrum of the cavity is given in this by case:

\[
P(t) = \frac{P(\omega_0)}{1 + q^2 \sin^2(\omega_m t)},
\]

where \( q = \Omega / \Gamma \) is the ratio between the modulation amplitude \( \Omega \) and the FWHM line width of the non-modulated power spectrum \( \Gamma \). The only non zero components of the Fourier transform of this signal are those with even \( a \)-coefficients:

\[
P(t) = \frac{1}{2} a_0 + \sum_{n=1}^{\infty} a_n \cos(n\omega_m t) + \sum_{n=1}^{\infty} b_n \sin(n\omega_m t)
\]

The authors also showed that the ratio between two next coefficients ‘r’ is constant and related to the Q factor by the relation:
Figure 3.4: Block diagram of the experimental setup used for microwave conductivity measurements.

\[ Q = \frac{\omega_0}{\Omega} \frac{\sqrt{r}}{1 - r} \quad \text{(3.8)} \]

In our setup, the frequency modulation of the microwaves emitted by the source (Agilent Technologies HP 83751) is controlled by a lock-in amplifier (Standford Research systems SR 830). The frequency of the modulation signal is 25.05 kHz, the amplitude $\Omega$ is approximatively equal to the line width of the unperturbed cavity $\Gamma$. 90 percent of the microwave power is transmitted by a coaxial cable to the cavity while 10 percent is sent to the frequency counter (Taked Riken TR5211 B). The radiation is coupled into the cavity laterally (see Fig. 3.3) and the absorbed power is measured in a transmission configuration by a solid state detector (Agilent Technologies 8474 C). The signal from the detector is sent to the AFC (automatic frequency control) system and to the lock-in amplifier to measure the second and the fourth harmonics.

The AFC system maintains the driving frequency of the cavity at the res-
onance frequency during the measurement. Its principal element is a second lock-in amplifier which measures the first harmonic of the cavity spectrum. This value is directly proportional to the frequency shift from the resonance value of the cavity. The output of the lock-in is a $dc$ signal added to the modulation signal which drives the microwave source to the cavity resonance frequency.
3.3 Electron spin resonance

3.3.1 Basic concepts

Although electron spin resonance (ESR) is still not as wide spread as nuclear magnetic resonance (NMR), it is a spectroscopic technique that is used in more and more research fields from biology to solid state physics. In the study of solid state phases ESR can give information about the electronic structure, magnetically ordered states and spin dynamics.

In this section the basic concepts of the ESR of paramagnetic phases will be briefly presented, with particular attention to those aspects that are of interest in the study of fulleride compounds.

A free electron has a magnetic moment parallel to its spin $S$:

$$\vec{\mu}_e = -g_e \mu_\beta \vec{S}$$  \hspace{1cm} (3.9)

where $g_e$ is the electronic $g$ factor ($g_e \cong 2.0023$) and $\mu_\beta$ is the Bohr magneton ($\mu_\beta = 9.274110^{-24} \text{ JT}^{-1}$).

An electron in an atomic shell has an angular moment $L$ besides the spin $S$. When the spin-orbit coupling $\lambda LS$, where $\lambda$ is the spin orbit coupling constant, can be neglected, $S$ and $L$ assume well defined values, given by the first two Hund’s rules. In this case, the magnetic moment of the electron is given by $\mu_\beta (L + g_e \vec{S})$. When the spin-orbit coupling cannot be neglected the only well-defined quantity is the total angular momentum $J$ given by the third Hund’s rule. Even in this case it is possible to define a magnetic moment of the electron $\mu_e$ which is parallel to the total angular momentum $J$ [53]:

$$\vec{\mu}_e = -g(JLS)\mu_\beta \vec{J} \hspace{1cm} (3.10)$$

Here the proportionality constant is the Landé $g$ factor which depends only on the $J, L, S$ quantum numbers of the electron in a given atomic shell. In both cases the interaction between an external magnetic field $\vec{B}$ and the magnetic moment of the electron can be expressed by the operator:

$$H = -\vec{\mu}_e \cdot \vec{B} = g\mu_\beta \vec{J} \vec{B}$$ \hspace{1cm} (3.11)

where $g$ is the free electron or the Landé $g$ factor. The eigenvalues of the operator when the magnetic field is directed along the quantization axis $z$ are given by:

$$E = g\mu_\beta Bm$$ \hspace{1cm} (3.12)

where $m$ is the eigenvalue of $J_z$ the $z$ component of the angular momentum operator $J$. Equation (3.12) shows that the main effect of the applied magnetic field is to split the electronic energy levels with different quantum number $m$. This effect is called Zeeman splitting. The energy levels for a spin $J = 1$ are shown in Fig. 3.5, the energy separation between two neighboring levels is $\Delta E = g\mu_\beta hB$. Resonance absorption of an electromagnetic radiation with frequency $\nu$ happens if the following condition is satisfied:
\[ h\nu = \Delta E = g \mu_B B \]  \hspace{1cm} (3.13)

Transitions with \( \Delta m \neq 1 \) have vanishing matrix elements and do not contribute to the ESR spectrum \cite{54}. Equation (3.13) states a direct proportionality between the applied magnetic field and the resonance frequency. In the usual experimental conditions the applied magnetic field is 0.3-15 T and the resonance frequency is in the microwave (GHz) frequency range.

![Figure 3.5: Zeeman energy levels of an electronic spin with angular momentum \( J = 1 \) in a magnetic field \( B \).](image.png)

From the point of view of classical physics an angular moment \( \vec{J} \) in a magnetic field follows the Newton’s law:

\[ \frac{d\vec{J}}{dt} = \vec{\mu} \wedge \vec{B} \]  \hspace{1cm} (3.14)

which can be rewritten using (3.10) in the following form:

\[ \frac{d\vec{\mu}_e}{dt} = g \mu_B (\vec{B} \wedge \vec{\mu}_e) \]  \hspace{1cm} (3.15)

This equation describes a vector precessing around the direction of the applied magnetic field with frequency \( \nu = (g \mu_B B) / h \) called Larmor frequency. The precessing magnetic moment can absorb energy from a microwave radiation oscillating at the Larmor frequency in phase with the precession motion. This result is in agreement with the quantum-mechanical description of the resonance absorption confirming the validity of both approaches. In a real system an ensemble of electrons interacts not only with the external magnetic field and the microwave radiation but also with the surrounding environment (e.g. the crystal lattice). While the resonance absorption of radiation induces transitions between energy levels and equalizes the spin populations, the interaction with the environment drives the spins to thermodynamic equilibrium.

All the spins that precess around the direction of the applied magnetic field contribute to the magnetization \( M \) of the sample defined as the magnetic moment per unit volume. Postulating an exponential relaxation of the components of the magnetization, the equations of motion assume the form [55]:
\[
\begin{align*}
\frac{dM_x}{dt} &= g\mu_B(M \times B)_x - \frac{M_x}{T_2} \tag{3.16a} \\
\frac{dM_y}{dt} &= g\mu_B(M \times B)_y - \frac{M_y}{T_2} \tag{3.16b} \\
\frac{dM_z}{dt} &= g\mu_B(M \times B)_z - \frac{M_z - M_0}{T_1} \tag{3.16c}
\end{align*}
\]

Here \(T_1\) is the spin-lattice relaxation time while \(T_2\) is the transversal relaxation time and represents the time during which the spins that contribute to the magnetization \(M\) precess in phase. \(B(t) = B_0\hat{z} + B_1(t)\) is the applied magnetic field. If the amplitude of the alternating magnetic field \(B_1(t)\) is small it is possible to obtain the expression of the time dependent transversal magnetization \(M_x\) in the laboratory frame: \(M_x = 2(\chi' \cos(\omega t) + \chi'' \sin(\omega t))B_1\) where \(\omega\) is the angular frequency of the microwaves. \(\chi'\) and \(\chi''\) are the real and the imaginary parts of the complex dynamic susceptibility and can be expressed in the form:

\[
\begin{align*}
\chi' &= \frac{\chi_0}{2}\frac{\omega_0 T_2}{\omega_0 - \omega} \frac{(\omega_0 - \omega)T_2}{1 + (\omega_0 - \omega)^2T_2^2} \tag{3.17a} \\
\chi'' &= \frac{\chi_0}{2}\frac{\omega_0 T_2}{\omega_0 - \omega} \frac{1}{1 + (\omega_0 - \omega)^2T_2^2} \tag{3.17b}
\end{align*}
\]

where \(\chi_0\) is the static susceptibility and \(\omega_0\) is \(2\pi\) times the Larmor frequency. Equation (3.17 a,b) are the expression of a Lorentzian line and of its Kramers-Kronig pair. In a conventional ESR measurement \(M_x\) is the quantity which is directly measured and eqs. (3.17) describe the shape of the resonance line in the case of homogeneous broadening. For experimental reasons, ESR spectra are usually obtained by irradiating the sample at a fixed frequency and sweeping the value of the static magnetic field to fulfill the resonance condition (3.13). From the value of the resonance field it is possible to extract the value of the \(g\) factor which depends on the electronic configuration. The line width gives information about the spin-relaxation times \(T_1\) and \(T_2\). The intensity of the spectrum is related to the static susceptibility of the sample as will be shown in the following section.

### 3.3.2 Static susceptibility measurements

In the framework of the linear response theory it can be shown that the microwave power \(P\) absorbed is given by:

\[
P = \frac{1}{2}B_1^2\omega\chi''(\omega)V \tag{3.18}
\]

where \(B_1\) is the amplitude of the microwave field of angular frequency \(\omega\) and \(V\) is the volume of the sample. Using the Kramers-Kronig relations it is possible to show that when the resonance line is narrow compared to the resonance angular frequency \(\omega_0\), the static susceptibility \(\chi(0)\) is related to the imaginary part of the dynamic susceptibility by the following relation:
\[
\chi'(0) = \frac{1}{\omega_0} \int_{-\infty}^{\infty} \chi(\omega) d\omega
\]

where \(\omega_0\) is the resonance angular frequency. Substituting this expression in eq. (3.18) a relation between the intensity of the absorption line, \(A\) and the static susceptibility is obtained:

\[
A = \int_{-\infty}^{\infty} P(\omega) d\omega = \frac{1}{2} B_1^2 V \omega_0^2 \pi \chi(0)
\]

The value of the microwave field amplitude \(B_1\) at the position of the sample is difficult to evaluate in most experimental situations. This uncertainty can be avoided by dividing the intensity of the signal with that of a reference material in the same position in the wave guide as the sample, with a known static susceptibility value \(\chi_2(0)\). Indicating the intensity of the ESR signal of the sample by \(A_1\) and those of the reference material by \(A_2\), the static susceptibility is given by:

\[
\frac{A_1}{A_2} = \frac{V_1 \chi_1(0)}{V_2 \chi_2(0)}
\]

The temperature dependence of the static susceptibility gives indications about the electronic structure of the sample. The susceptibility of insulating phases, in which the spins are localized, increases with the lowering of the temperature following the Curie formula [53]:

\[
\chi(0) = N \frac{(g \mu_B)^2}{V} \frac{J(J + 1)}{k_B T},
\]

where \(N\) is the number of spins in the volume \(V\). On the other hand the susceptibility of a metallic phase is constant for \(T\) much lower than the Fermi temperature. Its value is a function of the density of states at the Fermi energy, \(D(E_f)\), and of the \(g\) factor as given by the Pauli formula [53]:

\[
\chi(0) = \frac{1}{4} g^2 \mu_\beta^2 D(E_f)
\]

When electron-electron interactions are important, as for most fulleride compounds the Pauli formula, for the susceptibility is no more valid. A simple description of the magnetic susceptibility of a correlated electron gas is given by the Hubbard model described in chapter 2 in which the Coulomb interaction is described by the onsite \(U\) energy parameter. The solution of the problem, within the mean-field approximation, is given by the Stoner formula of the susceptibility \(\chi\) of the correlated metal:

\[
\chi = \frac{\chi_p}{1 - U \chi_p}
\]

where \(\chi_p\) is the Pauli susceptibility of the free electron gas. Eq. 3.24 states that the Coulomb interaction between the electrons increases the susceptibility of the electron gas.
ESR measurements of the static susceptibility are particularly suitable to
determine the static susceptibility in multiphase samples. Different phases
usually give different absorption lines in the ESR spectrum and this allows
to separate their contribution to the overall susceptibility of the sample.

It is important to observe here that Eq. 3.18 is valid only when the micro-
wave radiation intensity is small enough to avoid the inversion of popu-
lation between the Zeeman levels (see Fig 3.5). At high power levels deviations
from Eq. 3.18 are observed and the intensity of the ESR line starts to de-
crease with increasing irradiating microwave power. This condition is called
saturation of the absorption line and has to be careful avoided in typical
measurements.

3.3.3 Anisotropic $g$ factor and powder spectrum

The electronic configuration of a magnetic ion in a crystal lattice is modified
by the electrostatic field arising from the neighboring atoms, the crystal field
[54]. The new electronic states are the solutions of the following Hamiltonian:

$$
H = \sum_{i} \left( \frac{p_{i}^{2}}{2m} + V_{0i} \right) + \mu_{\lambda} (\vec{L} + g_{e}\vec{S})B_{0} + V_{1} + \lambda \ell S \quad , \quad (3.25)
$$

where $p_{i}$ is the momentum of the electron, $V_{0i}$ is the free ion potential, $\mu_{\lambda} (\vec{L} + g_{e}\vec{S})B_{0}$ represents the Zeeman interaction, $V_{1}$ is the crystal field and $\lambda \ell S$ is
the spin-orbit coupling. The crystal field and the spin orbit coupling terms
can be treated as perturbations with respect to the first two terms. The
solution of this problem for different crystal fields is given in [56].

In general, electronic orbitals with higher energy are mixed to the ground
state by the crystal field. The admixture depends on the crystal field symme-
try and it can result in an anisotropic ground state wave function. Together
with spin-orbit coupling may yield an anisotropic $g$ factor.

This anisotropy is reflected in the dependence of the resonance field on
the relative orientation of $B_{0}$ and the crystal axes in ESR experiments made
on single crystal samples. Formally the resonance condition can still be
expressed in the form (3.12) where $g$ is a tensor and not a scalar quantity.

In powder samples all the possible orientations between the crystallites
and the magnetic field are present. When the interaction between the mag-
netic ions is small and all the ions are symmetrically equivalent, the $g$-factor
anisotropy affects the shape of the resonance line which shows two or three
singularities in the case of biaxial and 3-axial symmetry respectively. This
particular absorption line is called powder-spectrum and an exact analytical
expression of it is given in [54]. A real spectrum is given by the convolu-
tion of the powder-spectrum distribution of the resonance field due the $g$-factor
anisotropy and a Lorentzian line arising from the relaxation mechanism de-
scribed by the Bloch equations. In Fig. 3.6 the derivative of two powder
spectra are shown.
3.3.4 Dipole-dipole broadening - the Van-Vleck formula

The presence of other magnetic ions in the lattice can also influence ESR. In the simplest case the spin sees the sum of the external applied field and of the dipolar field induced by the neighboring ions. At high temperatures, this interaction has no effect on the position of the resonance field but the broadening of the absorption line $\Delta H$ can be estimated from the Van-Vleck formula:

$$\Delta H^2 = \frac{1}{3} (g_{\mu_B})^2 \hbar^2 S(S+1) \frac{1}{N} \sum_{k,l} \frac{(1 - 3 \cos^2 \theta_{kl})^2}{r_{kl}^6} , \quad (3.26)$$

for like spins, where $\theta_{kl}$ is the angle between the direction of the applied magnetic field and the direction of the vector which connects the two spins at distance $r_{kl}$.

3.3.5 Electron spin resonance in metallic phases

In metallic phases the ESR arises from the conduction electrons. The shape of the resonance line depends on the conductivity and the dimensions of the sample. If the characteristic dimension of the sample is much less than the penetration depth, the microwave field seen by the electrons is constant and the absorption line is well described by a Lorentzian. In the opposite case the penetration of microwaves is limited to the skin depth. The microwave field amplitude and phase seen by the conducting electrons change significantly on the scale of the skin depth. The absorption line shape in this case is no more Lorentzian and assumes the form of a Dysonian [57, 58]. The intensity of the line is temperature independent, as seen in the precedent paragraph, except for the case in which the skin depth varies with $T$.

In pure metals the spin relaxation times $T_1$ and $T_2$ are usually equal and determined by the modulation of the spin-orbit coupling by phonons [59]:

$$\frac{1}{T_1} = \frac{\alpha(\Delta g)^2}{\tau} . \quad (3.27)$$
\( \alpha \) is a constant which depends only on the material, \( \tau \) is the electron phonon scattering time and \( \Delta g \) is the deviation of the \( g \) factor from the free electron value [60, 61]. This results in a line width which is directly proportional to the electrical resistivity. Above the Debye temperature, the line broadens linearly with \( T \).

Due to the motion of the electrons, ESR in a metallic phase is averaged on a scale equal to the spin diffusion length \( \delta \). If the electrons diffuse in three dimensions: \( \delta^2 = 1/3v_f^2\tau T \) where \( v_f \) is the Fermi velocity of the electrons. \( \delta \) can be estimated by substituting \( T_1 \) from eq. (3.27) with \( \alpha = 1 \) and recognizing that \( v_f \tau = d \) is the mean free path:

\[
\delta = \frac{1}{\sqrt{3}} \frac{d}{\Delta g} .
\]  

(3.28)

In multi phase materials electrons can diffuse between two neighboring metallic phases and have common ESR absorption line. The \( g \) factor and the line width of the absorption line is the average of the values of the isolated phases weighted by the fraction of times, \( f \) and \( (1 - f) \), spent by the electrons in each phase:

\[
g = fg_1 + (1-f)g_2 \tag{3.29a}
\]

\[
\Delta H = f\Delta H_1 + (1-f)\Delta H_2 . \tag{3.29b}
\]

### 3.3.6 Motional narrowing of the resonance line

In this paragraph the effect of the motion of the spin on the ESR line width will be treated following the simplified approach presented in [62]. This effect will be of particular interest in the discussion of the measurements on the \( \text{Li}_4\text{C}_6\text{O}_{16} \) fullerene polymer. A spin in a magnetic field \( B \) precesses at the Larmor angular frequency \( \omega = g\mu_B B \). In a crystal the spin interacts also with local fields \( B_{\text{loc}} \) arising e.g. by the dipole interaction with the neighboring magnetic ions. If the spin diffuses with a characteristic hopping time \( \tau \) the local magnetic field varies in time. Treating the problem as a random walk process, this interaction induces an extra phase in the precession \( \Delta \phi = g\mu_B B_{\text{loc}} \tau /h \).

After \( n \) jumps the dephasing will be: \( \langle \phi^2 \rangle = n(g\mu_B)^2B_{\text{loc}}^2\tau^2 \). Spins which precess with a dephasing more than one radian do not contribute to the resonance line. This will happen after \( N = ((g\mu_B)^2B_{\text{loc}}^2\tau^2)^{-1} \) in a time \( T_2 = N\tau = ((g\mu_B)^2B_{\text{loc}}^2\tau)^{-1} \). The line width expressed as \( \Delta \omega \) is given by:

\[
\Delta \omega = 1/T_2 = (g\mu_B)^2\tau = (\Delta \omega_0)^2\tau \tag{3.30}
\]

Equations 3.30 shows that if \( (\Delta \omega_0)\tau \ll 1 \) the line will be narrowed by the spin diffusion.

It is interesting to consider the case in which the spin motion sets in gradually with the temperature (e.g. thermally activated process) [54]. For simplicity we analyze spins that have two different states, for example two different orientations with respect to the magnetic field in a bi-axial \( g \)-factor.
anisotropic sample or two different phases between which the electrons can diffuse. When the spins are static, two lines are visible in the ESR spectrum. When the motion sets in, the lines first broaden and $g$ factors get closer to each other. At higher diffusion rates a third absorption line appears. This line is the motionally narrowed line arising from the faster ions. As the rate further increases, the intensity of the motional narrowed line grows while those of the "static absorption lines" disappear.

### 3.3.7 X-band ESR spectrometer

Microwave technology (i.e. sources, detectors and transmission lines) is particularly well developed in the frequency range about 9 GHz. The long wave length at these frequencies (about 3.3 cm) allows the use of resonant cavities of comfortable dimensions in which samples of typical dimensions of a few mm can be inserted. As presented in Sec. 3.2.1, the microwave radiation is multiply reflected giving rise to a standing waves pattern called mode. The average energy density in the cavity is approximatively $Q$ times higher than in the wave guide. This induces an increase of the ESR signal intensity which is directly proportional to the square root of the incident power.

![Figure 3.7: Schematic view of a 9 GHz ESR spectrometer (from Bruker).](image)

The ESR signal is detected with the help of a microwave bridge which
is schematically shown in fig. 3.7. In a microwave bridge a fraction of the power emitted by the source (a Gunn diode) is sent to the resonant cavity that contains the sample and the rest is sent directly to the detector through the "reference arm". The amount of microwave radiation that enters the cavity from the wave guides can be tuned with the help of a coupling element (the iris). The cavity is "critically coupled" when the coupled power equals to the power dissipated as Joule heat in the cavity walls. In this case no microwave radiation is reflected by the cavity. At ESR microwaves are absorbed in the sample and the cavity is no more critically coupled. Some of the microwaves is reflected from the cavity and measured by the detector. Detector sensitivity depends on the amount of microwaves that reaches it so some microwave power from the reference arm biases the detector to the ideal working point.

At 9 GHz the resonance magnetic field for a sample with $g$ factor equal to 2 is about 0.3 T and this is obtained with a resistive coil. The magnetic field is modulated with a frequency of 100 kHz using a second small coil. This modulation is driven by a lock-in amplifier that detects the signal at the modulation frequency. Due to the field modulation the detected signal is the derivative ESR spectrum.

### 3.3.8 The high frequency "wave-guide" ESR spectrometer

The high frequency "wave-guide" spectrometer operates at 35, 75, 150 and 225 GHz. The resonance field at 225 GHz for a sample with $g$ factor equal to two is 8 T. This high magnetic field is obtained by a superconducting coil. The ESR signal intensity (see eq. (3.18)) and the sensitivity of the detector increases with the frequency and this compensates the lack of a microwave cavity which would impracticel at these wave lengths ($\lambda = 4/3 \text{ mm}$ at 225 GHz).

The microwave source is a quartz oscillator stabilized Gunn diode (Radiometer Physics) with a 50 mW output power at 75 GHz. The insertion of a doubler or a tripler allows to change the output frequency to 150 and 225 GHz. The outgoing microwaves are fed into an oversized 8 mm wave guide where they propagate with many different modes.

The static magnetic field is obtained with a Nb$_3$Ti superconducting coil (Oxford Instruments) and can be swept from 0 to 9 T. The sample is positioned in the center of the coil where the homogeneity of the magnetic field is about 10 ppm/cm. As in the 9 GHz spectrometers, the magnetic field is modulated for the lock-in detection by a small copper coil which surrounds the sample. The current in the modulation coil is generated by a Voltage/Current converter driven by the lock-in amplifier.

The sample space in the magnet is surrounded by a variable temperature insert in which it is possible to condensate liquid He from the reservoir of the superconducting coil. This allows to reach the temperature of 2 K under dynamic vacuum. The temperature of the sample can be raised up to 530 K with the help of a thermally isolated probe head.

The spectrometer can operate in both transmission and reflexion modes.
The ESR signal is detected by a liquid He-cooled InSb bolometer (QMC) and collected by the computer.

3.3.9 The high frequency "quasi optical" ESR spectrometer

The sensitivity of the high frequency "wave-guide" spectrometer was limited mainly by the low emitted power of the source at the highest frequency (225 GHz) and by the transmission losses in the oversized wave guides. The wave guides cannot be shortened under a certain critical length at which the source would be damaged by the magnetic field of the superconducting coil. The absence of a microwave "bridge" used in the 9 GHz spectrometers also limits the sensitivity of the detector which cannot be maintained at the ideal working point. For these reasons, a new microwave source was acquired in 2007 and the oversized wave guides were replaced by a quasi-optical bridge.

In such systems microwaves propagate from the source to the probe-head freely in space as Gaussian beams. This name derives from the Gaussian spatial distribution of the electric field amplitudes $E$ in the plane orthogonal to the direction of propagation. For a beam propagating along the $z$ direction $E$ is given by:

$$E = E_0 \exp\left(-\frac{x^2 + y^2}{w^2}\right).$$

(3.31)

The wave front $w$ of a Gaussian beam diverges during propagation along a $z$ direction from the minimum value $w_0$ at the aperture of the source to the
value \( w \) given by:

\[
w^2 = w_0^2[1 + \left( \frac{z^2}{z_0^2} \right)] ,
\]

where \( z_0 = (\pi w_0^2/\lambda) \) and \( \lambda \) is the wave length of the beam. The wavefront is flat at the beam waist \( w_0 \) and varies as a spherical wave with radius \( R \) with propagation:

\[
R = z[1 + \left( \frac{z^2}{z_0^2} \right)] .
\]

The beams can be focused by off-axis parabolic aluminum mirrors. Beam splitting and polarization selection is obtained with rotatory wire grids (see Fig. 3.9). The wire grids reflect the waves with the E-field parallel to the wires and are transparent to the orthogonally polarized ones. The attenuation is about 0.1 dB for the parallel polarized waves and 30 dB for the perpendicular ones. The polarization of a beam can be rotated with the help of ferromagnetic plates. The rotation angle is a function of the thickness of the plate, different rotation angles can be obtained with different plates.

Figure 3.9: Picture of a rotating wire grid used in the quasi optical spectrometer. The grid is transparent to waves with the E-field polarized orthogonally (T) to the direction of the wires (black arrows). Waves with parallel (R) polarization are reflected.

A picture and a schematic view of the system (Thomas Keating Ltd.) is shown in Fig. 3.10. Microwave radiation is produced by a phase locked oscillator oscillating at 13.9 GHz (Virginia Diodes). A series of doublers raise the output frequency to 222.4 GHz. The microwave source used in the previous set up can also be employed for samples which do not have sensitivity problems.

At the output of the source a corrugated horn (1) converts the microwave mode propagating in the conventional wave guide into a linearly polarized Gaussian beam with polarization angle of 45 degree with respect to the plane of the optical table (red beam). In microwave transmission systems it is important to avoid the formation of standing waves. This is achieved with the
Experimental methods

insertion of an isolator after the source. The isolator is a component that allows the transmission of the microwave in one direction only and absorbs the microwaves which propagate in the opposite one. Here, this is realized with a grid and a ferromagnetic rotator. The orientation of the grid is perpendicular to the polarization of the direct beam. The rotator turns the polarization of the direct beam by -45 degree so that it becomes vertical to the plane of optical table. The polarization of a beam propagating in the opposite direction is rotated +45 degree and is reflected by the grid into an absorber.

After the isolator the beam is separated by a beam splitter (3) into the reference (light blue) and sample (red) arms. The reference is sent directly to the detector (4), after a 90 degree rotation of its polarization, to define the working point. The sample arm is sent to the probe head. In the sample arm two attenuators and a phase shifter finely tune the power and the phase of the microwave radiation. At the entrance of the magnet the beam is coupled into a HE11 corrugated wave guide through a polyethylene window. The guide is a thin walled (300 micron) corrugated tube made of German silver, a material with very low thermal conductivity. The corrugations have a depth of $\lambda/4$ and a spacing of $\lambda/2$. This corrugation induces a very high wall impedance to the mm-wave radiation, while keeping the wall currents and so the dissipation very low. The tube preserve the polarization of the radiation.

Microwaves pass through the sample and are reflected from a mirror at the end of the probe head. The fraction of the microwave beam which suffers ESR absorption acquires a circular polarization. This can be understood considering that a linearly polarized field is the sum of two circularly polarized components which rotate in the opposite direction [54]. Only the component that rotates in phase with the spin precession is absorbed while the other is reflected. The outgoing beam is sent to a grid which transmits only the component with polarization orthogonal to the incident beam. This way we filter out the direct beam and only the part that suffered ESR (dark blue) is allowed to reach, from the microwave radiation which has not suffered ESR (green beam). The ESR signal is added to the reference arm and sent to the detector.

Two detectors can be used to detect the ESR signal: a liquid Helium cooled InSb bolometer (QMC instruments) (5) or a solid state detector (Millitech) (6). The solid state detector has a sensitivity comparable to the Bolometer at 111.2 GHz and 75 GHz with no need of liquid He cooling.

The divergence of a Gaussian beam increases with decreasing frequency. The maximum beam width is reached at the focusing mirror and is equal to 14 mm at 222.4 GHz. At frequencies lower than 75 GHz the beam width becomes comparable to the dimension of the mirror inducing high losses. The rotation angle of the ferromagnetic rotators is also a function of the frequency and cannot be used at frequencies lower than 111.2 GHz. The sensitivity test of the spectrometer indicated 75 GHz as a lower limit for the usable frequency of the optical bridge.

Previous experience on similar experimental setups in Lausanne suggested
the importance to isolate the spectrometer vibrationally. Relative displacements between the magnet and the optical bridge results, in fact, in a change of the optical path which induces a noise at the detector. At 222.4 GHz the wave length is 1.3 mm so even small displacements change the amplitude of the microwave fields at the detector and add to the noise. The typical ESR signal amplitude (10^{-6} \text{ V}) detected by the lock-in amplifier is very small compared to the overall microwave signal at the detector (10^{-1} \text{ V}).

For these reasons, we placed the spectrometer on a vibration-isolated supporting structure shown in Fig. 3.11. The supporting structure was designed in collaboration with Dr. Reis of the Building Acoustic Laboratory and Dr. Kiss and Dr. Hunyadi of the Structural Department of the BME. Ferromagnetic materials which could influence the homogeneity of the magnet were avoided. The magnet (1) is placed on a 2-ton C38 concrete mass (4) which is isolated from the ground by 36 copolymeric blocks (CDM) (5). The optical bridge is sustained by an aluminum structure (ITEM) (3) on the top of 4 brick columns strengthened by aluminum shafts. The aluminum structure can be shifted horizontally with the help of a linear roller guide to allow the extraction of the probe head from the magnet. The self resonant frequency of the structure is only 10 Hz. At higher frequencies the structure damps efficiently mechanical vibrations.

3.3.10 The probe head

A schematic view of the end of the probe head is shown in Fig. 3.12. Microwave horns [1] with different ending diameters (3.8, 7 mm) (Thomas Keating Ltd) focus the microwaves onto the sample. With an additional element [2], it is possible to focus the microwave front to 1.9 mm. The sample is positioned in a copper Helmotz coil for the modulation [3]. The coil is inserted in a copper cylinder [4] which allows thermalization and contains the heating resistance and the temperature sensor. With the help of a screw that can be rotated during the measurement [6] it is possible to move a mirror [5] on the bottom. This allows to position the sample to the antinodes of the standing waves in the sample holder. To avoid vibration induced by the alternating current flowing in the modulation coil, great attention was paid to the mechanical coupling between the coil and the copper cylinder.

3.3.11 The spectrometer performance

The sensitivity of the spectrometer measured using MgO doped with 1.5 ppm of Mn^{2+}, a standard ESR reference is 3 \times 10^{10} \text{ spins} / (10^{-4} \text{ T\cdot s}) at 300 K. This value is one of the highest reported for spectrometers operating in this frequency range without a resonant cavity. Its value is comparable with those of the best commercial 9 GHz ESR spectrometers which use a resonant cavity. The line width of the Mn^{2+} lines is about 0.1 mT in both the 8 T and 0.3 mT field measurements confirming that the high homogeneity of the magnet is not influenced by the supporting structure of the optical bridge (see Fig. 3.13). The mechanical stability of the spectrometer is demonstrated by the
perfectly flat base line of the spectrum of orthorhombic KC$_{60}$ shown in Fig. 3.13.

3.4 Other experimental techniques

3.4.1 SQUID magnetometry

Measuring with sufficient precision the intensity of the ESR signal could be difficult in samples with a broad spectrum which overlaps the absorption line of the commonly used reference materials. In these cases the static susceptibility can be measured by a SQUID (Superconducting QUantum Interferometer Device) magnetometer. The magnetization of the sample can be obtained as function of temperature or magnetic field intensity. The measurements reported in the following chapters were made by Laszló Kiss (SZFKI) with a commercial Quantum Design MPMS-5S SQUID magnetometer.

3.4.2 Infrared and Raman spectroscopies

Important informations about the structure of the fullerides can be obtained from their phonon spectrum. Due to the nature of molecular solids, fullerides have both intermolecular and intramolecular vibrating modes (see Chapter I). The most used experimental techniques to study the phonon modes are infrared spectroscopy and Raman scattering. Due to the high symmetry of the fullerene molecule only 4 modes are infrared active and 8 Raman active. The number of observable modes increases when the symmetry of C$_{60}$ is distorted, e.g. in the case of fulleride polymers.

Infrared transmission spectra were recorded on pellets of sample powder diluted with KBr under dynamic vacuum. The measurements were performed in the laboratory of Dr. Katalin Kamarás (SZFKI) with a Bruker IFS 28 FTIR spectrometer.

Raman spectra were collected in Milan at the Laboratory of Prof. Bottani (Politecnico di Milano, Milan) using a T64000 Jobin-Yvon spectrometer.
Figure 3.10: Picture (upper panel) and schematic view (lower panel) of the quasi-optical bridge. The dashed rectangle indicates the part of the scheme which is visible on the picture. The gray triangles represent the focusing mirrors, the continuous lines the wire grids, the dashed lines the rotating wire grids. The red color indicates the direct beam (from the source to the sample) the green the reflected beam (from the sample to the absorber) the light blue the reference arm, the dark blue the ESR signal. The polarization of the beams is given with respect to the plane of the optical table with the letters v (vertical) and h (horizontal). (1): microwave source, (2) isolator, (3) beam splitter, (4) phase shifter, (5,6) detectors, (7,8) attenuators, (10) polythene window of the probe head, (11) sample. The reflected microwaves are separated from the ESR signal with the wire grid (9)].
Figure 3.11: Overall view of the "quasi optical" high frequency ESR spectrometer. (1) magnet, (2) detector, (3) aluminum supporting structure, (4) concrete block, (5) copolymeric spring
Figure 3.12: Schematic view of the end part of the probe head. (1): microwave horn, (2) additional focusing element, (3) modulation coil, (4) thermalising copper block, (5) movable mirror, (6) positioning screw.

Figure 3.13: Left: ESR spectrum of Mn:MgO with a Mn concentration of 1.5 ppm measured at 9 GHz with a commercial spectrometer (black spectrum) and at 222.4 (red spectrum) with the quasi optical spectrometer. Right: 222.4 GHz ESR spectrum of orthorhombic KC₆₀, the base line of the spectrum is flat.
Chapter 4

Phase segregation in KC$_{60}$ and Na$_2$C$_{60}$

4.1 Introduction

The determination of the exact crystal structure is one of the most difficult tasks in the study of alkali intercalated fullerenes. As we mentioned in Chap. 2, the phase diagram of these materials is complex and many competing mechanisms play a role in determining their structure. In this chapter, we discuss two fullerenes, KC$_{60}$ and Na$_2$C$_{60}$, whose crystal structures are strongly influenced by the diffusion of the intercalated cations in the lattice. In both materials, there is a temperature range in which domains with composition different from the nominal one are observed. The characteristic dimension of these domains is about 10 nm in KC$_{60}$ and somewhat smaller in Na$_2$C$_{60}$ (3-10 nm). The cationic concentration in the segregated domains is almost perfectly stoichiometric in the case of KC$_{60}$, while in Na$_2$C$_{60}$ is less defined.

The study of phase segregated fullerenes is difficult. The absence of long range order and low sensitivity limits X-ray diffraction. For example, in Na$_2$C$_{60}$, the different phases are so finely distributed that only an average structure is observed. Magnetic resonance methods like NMR and ESR are more suitable although NMR sensitivity is in some cases insufficient to observe all phases. Conventional 9 GHz ESR spectrometers have a 2-3 order of magnitude higher sensitivity than NMR but they are limited by the low spectral resolution. Different segregated phases have similar g factors and their absorption lines cannot be resolved in low field ESR measurements. Conductivity measurements are difficult on samples which are usually available as powder or small crystals only.

Here we show that phase segregation can be detected with HF-ESR and microwave conductivity measurements. HF-ESR spectrometers have enough sensitivity and spectral resolution to detect minority phases. High sensitivity can be reached even in metallic fullerenes where the skin penetration depth in the microwave frequency range is much lower than the typical grain size (10-100 microns). Microwave conductivity measurements are particularly suitable for air-sensitive powders and are equivalent to dc ones for fullerenes in which the plasma frequency is about 250 THz. Structural changes and
inhomogeneities of the sample influence the electric properties and can be studied by measuring the temperature dependence of the microwave conductivity.

A study of the depolymerization of orthorhombic KC$_{60}$ demonstrates that these experimental techniques are suitable to investigate phase segregations in fullerenes. Our measurements are in agreement with those reported in the literature and clarify some aspects of the morphology of the phase distribution. Second, we study the phase homogeneity of Na$_2$C$_{60}$ with HF-ESR and we observe phase segregation below 450 K. Our results, in addition to infrared spectroscopy, NMR and neutron diffraction measurements, clarify the mechanism of the segregation and the electronic and magnetic properties of the resulting phases.

4.2 Depolymerization of orthorhombic KC$_{60}$

4.2.1 Previous results

The discovery of superconductivity in K$_3$C$_{60}$ (T$_c$ = 19.3 K) [3] raised the interest in the alkali intercalated salts. A large number of studies were conducted to understand the phase diagram of K$_3$C$_{60}$ systems. In 1994, it was discovered that the orthorhombic phase at composition of x=1, α-KC$_{60}$, is a (2+2) cycloadducted one-dimensional (1D) fulleride polymer [23, 27, 28] (see Sec. 2.3.4). α-KC$_{60}$ is stable in air [63], and it interestingly has a metallic ground state [44].

At higher temperatures, KC$_{60}$ depolymerizes and a monomeric rockstalt, cubic phase, α-KC$_{60}$, forms. Depolymerization of orthorhombic KC$_{60}$ is reversible with temperature and strongly influenced by the diffusion of the cation. Close to the depolymerization temperature the K$^+$ ions diffuse and phase segregate into pure C$_{60}$ and K$_3$C$_{60}$ domains [64]. This intermediate phase, i-KC$_{60}$, can be maintained in a metastable state at low temperatures by quenching below from $T > 400$ K to less than 360 K, the depolymerization temperature.

Quenching the high temperature monomeric phase below 270 K results in the formation of a second orthorhombic phase consisting of fullerene dimers [33]. At these temperatures the C$_{60}$ rotation is hindered and this prevents the molecules from assuming the reciprocal orientation required to form the (2+2) cycloadducted bonds of the polymeric structure (see Sec. 2.3.4).

4.2.2 Sample preparation

Orthorhombic KC$_{60}$ was prepared by Gyöngyi Klupp (SZFKI) by solid state reaction between C$_{60}$ and pure K powders under argon atmosphere in a dry box. The powder mixture was maintained at 623 K in a carbon steel container for 10 days. It was reground several times to obtain a homogeneous powder mixture. The sample was quenched from 353 K to avoid phase segregation.
4.2.3 High frequency ESR and microwave conductivity measurements

The ESR spectra were collected by heating as prepared o-KC$_{60}$ from 290 K to 525 K and cooling back. The temperature sweep rate was about 2 K/min. Five temperature ranges with different phase distributions can be identified. In Table 4.1 the different temperatures with the corresponding phase distributions described in the following are indicated.

The changes in the ESR spectrum with increasing temperature are shown in Fig. 4.1. The spectrum is composed of one line for $T < 430$ K (I–III). Above this temperature the intensity of the line decreases while a new line grows (IV–V).

<table>
<thead>
<tr>
<th>Range</th>
<th>Temperatures</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$T &lt; 360$ K</td>
<td>orthorhombic KC$<em>{60}$ (o-KC$</em>{60}$)</td>
</tr>
<tr>
<td>II</td>
<td>360 &lt; $T &lt; 390$ K</td>
<td>orthorhombic KC$<em>{60}$ + K$<em>3$C$</em>{60}$ + C$</em>{60}$</td>
</tr>
<tr>
<td>III</td>
<td>390 &lt; $T &lt; 420$ K</td>
<td>K$<em>3$C$</em>{60}$ + C$<em>{60}$ (intermediate KC$</em>{60}$)</td>
</tr>
<tr>
<td>IV</td>
<td>420 &lt; $T &lt; 450$ K</td>
<td>Rocksalt KC$<em>{60}$ + K$<em>3$C$</em>{60}$ + C$</em>{60}$</td>
</tr>
<tr>
<td>V</td>
<td>$T &gt; 450$ K</td>
<td>Rocksalt KC$<em>{60}$ (c-KC$</em>{60}$)</td>
</tr>
</tbody>
</table>

Table 4.1: Phase distributions in nominal KC$_{60}$.

The changes in the ESR spectrum are more evident in the temperature dependence of the resonance field measured on heating and cooling shown in Fig. 4.2.

In temperature range (I), the position of the line is temperature independent. In (II), the resonance field slightly decreases with temperature to 400 K. In (III), the resonance field increases with temperature while two lines are observed between 400 K and 425 K (IV). At higher temperatures, the spectrum shows only one absorption line (V).

The temperature dependence of the line width shown in Fig. 4.3 is also informative. In temperature range (I) the line broadens with $T$. The broadening in (II) is more pronounced and the line width reaches the value of 1.6 mT at 400 K. A second absorption line becomes visible in range (IV) while the first further broadens before disappearing. In the highest temperature range (V), the line width increases with $T$.

These results can be interpreted on the basis of those previously published [64]. First, we discuss the phase transitions observed with the increasing of the temperature. The polymeric phase is stable at temperatures below 360 K. Its metallic behavior is reflected in the linear temperature dependence of the line width. As mentioned in Sec. 3.3.5, the line width of metals in which the main relaxation mechanism is the electron-phonon scattering is directly proportional to the resistivity. At temperatures higher than $T_{\text{Debye}}$, the line is expected to broaden linearly with $T$.

The shift in the absorption line position at about 360 K indicates the beginning of structural changes related to depolymerization. The line broadening which accompanies the shift indicates an increased inhomogeneity of the sample. As depolymerization proceeds, K ions start diffusing and the
Figure 4.1: 225 GHz ESR spectra of KC$_{60}$ measured heating the sample from 300 K to 525 K. The five spectra correspond to different phase distributions as indicated in table 4.1.
Figure 4.2: Temperature dependence of the ESR absorption line position of \( \text{KC}_{60} \) measured heating the sample from 290 K to 525 K (black symbols) and cooling back (empty symbols).

first \( \text{K}_3\text{C}_{60} \) and pure \( \text{C}_{60} \) domains form. In the temperature range II three phases co-exist: \( \alpha\text{-KC}_{60} \), \( \text{K}_3\text{C}_{60} \) and pure \( \text{C}_{60} \).

The two ESR active phases, \( \alpha\text{-KC}_{60} \) and \( \text{K}_3\text{C}_{60} \), are metallic and have a common absorption line in the spectrum due to the diffusion of the conducting electrons between them. As the temperature increases, electrons spend more time in the enlarged \( \text{K}_3\text{C}_{60} \) domains. The ESR absorption line width in \( \text{K}_3\text{C}_{60} \) is larger, 0.14 mT at 350 K [65], than in \( \text{KC}_{60} \), 7 mT at 350 K, explaining the broadening of the ESR line in this temperature range.

At about 400 K, range (III), the depolymerization is complete and the sample is in the intermediate state. The ESR line arises from the isolated domains of \( \text{K}_3\text{C}_{60} \) in a \( \text{C}_{60} \) matrix.

At higher temperatures, in range IV, the new absorption line indicates the formation of the first c-\( \text{KC}_{60} \) domains. Similarly to temperature range II, two conducting phases exist in IV, c-\( \text{KC}_{60} \) and \( \text{K}_3\text{C}_{60} \). The two distinct absorption lines in the spectrum indicates that the conducting phases are isolated by insulating \( \text{C}_{60} \) domains and the electrons cannot diffuse between them.

In temperature range V, only the monomeric phase of \( \text{KC}_{60} \) remains. The slight shift in the ESR position with temperature is reversible and it is probably due to the thermal expansion of the lattice.

The intermediate phase does not form on cooling. The monomeric phase is unchanged at this cooling rate (2 K/min) down to the depolymerization temperature, 360 K. The formation of the first polymeric domains increases the line width of monomeric \( \text{KC}_{60} \) and the absorption line of the polymeric
Figure 4.3: Temperature dependence of the ESR line width of KC$_{60}$ for heating the sample from room temperature to 525 K (upper panel) and cooling back from the highest temperature (lower panel) with the same rate (2 K/min). At 360 K motional narrowing of resonances of monomeric and polymeric KC$_{60}$ domains merges the spectrum into one broadened line. Different symbols are used to indicate different absorption lines.
phase is broadened by the monomeric domains. This is expected since the two conducting phases are not separated by pure fullerite domains which form only in the intermediate state.

![Graph showing temperature dependence of microwave conductivity of KC60 normalized to the value at 300 K.](image)

Figure 4.4: Temperature dependence of the microwave conductivity of KC60 normalized to the value at 300 K. The minimum at 410 K signals the formation of intermediate KC60.

The phase transitions shown by HF-ESR measurements are observed in the temperature dependence of the microwave conductivity also (Fig. 4.4). Below the depolymerization temperature (about 360 K), $\sigma(T)$ slightly decreases with increasing $T$ as expected for a metal like o-KC60. In II, the sample is strongly inhomogeneous and the conductivity decreases with temperature to a minimum at 410 K. Above this temperature, o-KC60 is no more present and the microwave losses are due to K3C60 domains. At higher temperatures, the first cubic-KC60 domains appear increasing the inhomogeneity of the sample as confirmed by the second minimum around 440 K. Above 450 K, the activated behavior of the conductivity indicates the semiconducting nature of cubic KC60. The high temperature phase was overcooled to 340 K where it polymerizes.

Microwave conductivity was measured with a somewhat higher temperature sweep rate, 10 K/min, than HF-ESR. This explains the difference in the polymerization temperatures found by the two methods on cooling (360 K with ESR and 340 K with conductivity measurements).
4.3 Phase segregation in Na$_2$C$_{60}$

4.3.1 Previous results

A$_2$C$_{60}$ and A$_3$C$_{60}$ (A = K, Rb) fulleride salts have different ground states although the $t_{1u}$ conducting bands are only partially filled in both. The A$_3$C$_{60}$'s are superconductors while A$_2$C$_{60}$ fullerides have an insulating ground state. This different behavior was explained as a consequence of the interplay of the Jahn-Teller distortion of the charged fullerene molecules and the on-site Coulomb repulsion due to strong electron-electron correlations [37] as described in Sec. 2.5.2. The Jahn-Teller-Mott (JTM) insulating ground state was observed experimentally in K$_4$C$_{60}$ and Rb$_3$C$_{60}$ with electron energy loss spectroscopy [66] and NMR [67] and in Cs$_4$C$_{60}$ by neutron diffraction [68]. The Jahn-Teller distortion of the C$_{60}^{-}$ was proved by infrared measurements [69] and recently observed directly with Scanning Tunnelling Microscopy (STM)[70].

Na$_2$C$_{60}$ fulleride was intensively studied as a possible example of a JTM insulator. NMR and ESR [67] found the ground states of Na$_2$C$_{60}$ insulating and showed a low energy triplet excitation. A combined Raman and 9 GHz ESR study of Kubozono et al. [71] indicated instead a metal-insulator transition at 50 K. ESR studies at high temperatures (300-400 K) observed an hysteretic behavior of the absorption line.

These contradictory results motivated us to revisit the question of the ground state of Na$_2$C$_{60}$. With a combined infrared spectroscopy, NMR, HF-ESR and neutron diffraction study we showed that the unusual behavior of Na$_2$C$_{60}$ is a consequence of a phase segregation driven by the diffusion of the Na$^+$ ions that takes place at about 450 K. We observed at least three phases one of which is metallic. From the analysis of the IR spectrum we assigned the metallic phases to Na$_3$C$_{60}$. Of the two remaining phases one is assigned to C$_{60}$ intercalated with a low concentration of Na$^+$ ions while the composition of the other one remains indetermined. The inhomogeneity of the material explained the discordant results reported by the different groups. Different experimental methods are selectively sensitive to different phases. For example, the C$_{60}$ phase is difficulty observable by $^{13}$C NMR due to saturation and the interpretation of the 9 GHz ESR measurements was affected by the low spectral resolution.

4.3.2 High frequency ESR study

We studied the phases of nominal Na$_2$C$_{60}$ with HF-ESR. The presence of multiple phases results in an inhomogeneous broadening or in a split of the absorption line due to the difference in the $g$ factors.

The 225 GHz ESR spectrum measured at 225 K shown in Fig. 4.5 consists of three absorption lines. The three phases are visible at all temperatures between 4 and 450 K. The distance between the absorption lines are slightly temperature dependent and of the order of 0.10-0.20 mT. In a 9 GHz spectrometer, the spectral resolution is (225/9)=25 times lower and such small splittings could not be detected. The line widths of the three phases are
Figure 4.5: 225 GHz ESR spectrum of nominal Na$_2$C$_{60}$ at 225 K. The measured spectrum was fitted with three Lorentzian line (black, red an green lines). The sum of the three fitted components (light blue line) is also shown.

constant within the experimental precision at temperatures down to 100 K. Below this temperature, Phase 1 and 3 broadens from 2.2 mT to 3.2 mT and from 0.6 to 1.2 mT, respectively.

To avoid unwanted reactions between the ESR reference material and the sample, we used a small piece of $\alpha, \gamma$-bisdi phenylene-$\beta$-phenyl allyl (BDPA), as standard g-factor reference ($g=2.0025$) to calibrate the magnetic field. We normalized the full ESR intensity, $I_T$, to the static susceptibility measured by SQUID. The fractional intensity for each absorption line $I_i$, is proportional to the static susceptibility (see Sec. 3.3.2): $I_i = \chi_i V_i / I_T$, where $I_T = \Sigma I_i$ is the total ESR intensity, $\chi_i$, is the spin susceptibility and $V_i$ the fractional volume of the phase $i$. This allows to determine the temperature dependence of the spin susceptibility of the three phases (phase 1 to 3), shown in Fig. 4.6. We suppose that the volume of the different phases does not change with temperature. This hypothesis seems plausible for temperatures below 400 K where the Na$^+$ ions do not diffuse. The relatively large noise in the susceptibility data has to be ascribed to the difficulty in determining the intensity of Lorentzian lines when the splitting of the lines is comparable to the line widths as for Phase 1 and 2 (see fig. 4.5).

Static susceptibility of Phase 1 has a Curie-like temperature dependence corresponding to 1.3 % of $S = 1/2$ per C$_{60}$ molecules. Phase 2 is the phase with the largest spin susceptibility at $T > 175$ K while Phase 3 is the one with the smallest $g$ factor. The approximately temperature independent susceptibility indicates that Phase 3 is metallic. One possible explanation for the unusual temperature dependence of the static susceptibility of Phase
2 is that this phase is a mixture of phases with so small g factor differences that their lines are not resolved in the ESR spectrum.

![Graph showing temperature dependence of the spin susceptibility of different phases in nominal Na2C60. The continuous line indicates the full susceptibility of the sample.](image)

Figure 4.6: Temperature dependence of the spin susceptibility of the different phases in nominal Na2C60. The continuous line indicates the full susceptibility of the sample.

At 450 K a structural transition takes place, the three low temperature phases disappear and are replaced by a new one (see Fig. 4.7). The single Lorentzian ESR line indicates that an homogeneous material is formed. On rapid cooling (2.5 K/min) the sample is quenched into this metastable state. The original phase segregated material reappears after about two weeks at room temperature. The formation of the homogeneous phase for \(T > 450\) K and the possibility of preserving this phase at lower temperatures with a sufficiently fast cooling suggest that the structural transition is controlled by the diffusion of the Na+ ions.

To confirm this scenario we studied the temperature dependence of the HF-ESR spectrum of samples quenched with a higher cooling rate. The samples were heated from room temperature to 523 K, maintained at this temperature for 60 minutes and then quenched in liquid nitrogen. The temperature dependence of the ESR absorption line position measured between 5 and 250 K on quenched samples is shown in Fig. 4.7. The ESR spectrum is still composed of three absorption lines at \(T < 200\) K. Although the positions of the two lines are, within experimental accuracy, very similar to the those of Phase 1 and Phase 2 in the slowly cooled samples, the \(g\) factor of the third line is significantly different from those of Phase 3. The homogeneous material in this case is obtained at a lower temperature, 200 K, as demonstrated by the single absorption line ESR spectrum shown in Fig. 4.8. This indicates a finer distribution of the different phases formed by smaller...
Figure 4.7: ESR line position of the high temperature phases in nominal Na$_2$C$_{60}$. The three phase observed in the low temperature ranges disappear at about 450 K where the homogeneous phase forms.

segregated domains than in the slowly cooled samples. It was not possible to obtain a homogeneous material at lower temperatures.

4.3.3 Results of other methods

The HF-ESR results are in remarkably agreement with infrared spectroscopy (IR), NMR and neutron diffraction measurements [72]. IR is a particularly suitable technique for the study of the phonon modes in fulleride polymers. Only the four $T_{1U}$ intra molecular modes are active in the high symmetric C$_{60}$ molecule. The number of IR active modes increases in distorted C$_{60}$ molecules, as for example in polymers or Jahn-Teller distorted molecules.

Particularly interesting is the position of the $T_{1U}(4)$ mode (near 1428 cm$^{-1}$) of C$_{60}^{n-}$ anions which shifts proportionally to $n$. This allows to determine the charge state of the anions. IR spectra of Na$_2$C$_{60}$ have two $T_{1U}(4)$ absorption peaks which correspond to C$_{60}^{3-}$ anions and pure C$_{60}$ demonstrating the inhomogeneity of the sample. At temperatures above 470 K IR spectrum changes indicate a more homogeneous material with Jahn-Teller distorted C$_{60}^{2-}$ anions.

$^{13}$C NMR measurements confirmed the absence of amorphous carbon which would give a broad absorption line and detected at least two phases one of this was pure C$_{60}$. The absorption line of C$_{60}$ disappears at high temperatures as the homogeneity of the sample increases.

Neutron diffraction measurements indicated the onset of Na$^+$ ion diffusion above 400 K on a time scale of 0.8 ns. A jump distance of 4 Å was deduced.
Figure 4.8: 225 GHz ESR absorption spectrum of quenched Na$_2$C$_{60}$ samples at 200 K. The absorption line in the low magnetic field region is the field reference. The phases of the signals are different because the two samples were in different positions in the wave guide.
Figure 4.9: Temperature dependence of the 225 GHz ESR lines position of as prepared (red, green and black symbols) and quenched (blue symbols) \( \text{Na}_2\text{C}_{60} \) samples. \( T^\ast \) indicates the temperature above which the quenched sample is homogeneous.

This is the distance between the tetrahedral and an off-center octahedral site of the fullerite structure as shown in Fig. 4.10 [73].

4.3.4 Phase segregation in fulleride salts, general considerations

Although a rigorous analysis of the energy and entropy contributions involved in the phase segregations in fulleride salts is still missing, some general considerations can be done.

In both \( \text{K}_6\text{C}_{60} \) and \( \text{Na}_2\text{C}_{60} \) the formation of domains in the fullerene lattice with higher cationic content than the nominal one is driven by the gain in Coulomb energy (Madelung energy). This can be understood from the crystal structure of the fulleride salts, presented in Sec. 2.3.2. In absence of polymerization, the \( \text{C}_{60} \) molecules form an \( fcc \) lattice which has two tetrahedral and one octahedral voids per unit cell which can accommodate alkali atoms. A schematic view of the lattice is shown in Fig. 4.10. A cation in the tetrahedral, \( T \), site has four \( \text{C}_{60} \)'s first neighbors and six in the octahedral, \( O \), sites. The anion-cation distance in the \( T \) site is smaller than in the \( O \) site so the gain in Coulomb energy of an occupied \( T \) site is higher.

Light alkali cations, \( \text{A}_n \), in \( \text{A}_n\text{C}_{60} \) (\( n = 1, 2, 3 \)) can occupy off-center sites near the octahedral sites along the \( (111) \) crystalline direction [73]. The distance from the center of the octahedral site is higher for the light alkali cations (Li, Na and K). In the case of \( \text{Na}_2\text{C}_{60} \), for example, \( \text{Na}^+ \) cations occupy off-center
Phase segregation in $KC_{60}$ and $Na_2C_{60}$

sites in which they have the same distance from the first nearest neighbor fullerenes as in the tetrahedral sites. In phases with higher stoichiometry $C_{60}^{-2}$ anions coordinate more cations gaining in Coulomb energy. In $KC_{60}$, $K^+$ ions occupy only the octahedral sites while in $K_3C_{60}$ the tetrahedral sites are occupied also and this results in a gain in Coulomb energy. A similar mechanism happens when $Na_3C_{60}$ forms from $Na_2C_{60}$.

The cation-$C_{60}$ interaction in $A_3C_{60}$ Coulomb influences also the rotation of the fullerene molecules and favors the formation of an ordered $Fm\bar{3}m$ structure in which the molecules rotation is hindered (see Sec. 2.3.2). The low entropy associated to the inhomogeneous cation distribution and to the hindered rotations makes the segregated phase unstable at high temperatures. This drives the structural phase transition in both fullerenes. At high temperatures the distribution of the cations in the crystals becomes homogeneous and the $C_{60}$ molecules can rotate almost freely.

The cationic diffusion mechanism is the main difference between the phase transition in the two fullerenes. $Na^+$ ions move from a tetrahedral to an octahedral site of the fullerite structure along the (111) direction (see the potential in Fig. 4.10). K$^+$ ions are too large to diffuse through the trigonal aperture between the octahedral and the tetrahedral sites and some other mechanism as, e.g., the motion of dislocations or other defects have to be supposed. This explains why it is easier to quench the high temperature phase of $KC_{60}$ to a low temperature metastable state.

Figure 4.10: Illustration of the potential seen by a Na$^+$ (red circle) ion moving in the (111) direction of the fcc fullerene lattice (right). The blue circle represents a fullerene molecule.
Chapter 5

Metallic disordered fulleride polymers

5.1 Introduction

This chapter deals with the structural and magnetic properties of two fulleride polymers, Mg$_5$C$_{60}$ and K$_2$C$_{60}$C$_8$H$_8$. Although the two materials have different structures, both are characterized by strong disorder. Despite the disorder, the two materials are single-phase. The structural disorder is intrinsic, i.e. not due to an imperfect synthesis, and it strongly influences the electronic and magnetic properties. Both materials are metallic at room temperature and have a smooth transition to an insulating ground state at lower temperatures.

In the first paragraphs of the chapter, we present the results of the multifrequency ESR and microwave conductivity measurements in the two materials. The most important experimental observations about the localization of the electronic states are presented. In the last paragraph we discuss the experimental results and suggest that structural disorder gives rise to an Anderson localization of the electronic states.

5.2 The Mg$_5$C$_{60}$ fulleride polymer

5.2.1 Previous results

With the exception of the studies focused on superconductivity discussed in the Sec. 2.5.3, very few works deal with the synthesis and the physical properties of alkali-earth intercalated fullerenes. Interestingly, polymeric structures were not observed, in spite of theoretical predictions [24]. The only study of MgC$_{60}$ compounds reported on Mg intercalation of fullerite thin films [40].

The first systematic study of the phase diagram of the Mg$_x$C$_{60}$ system made at the Research Institute of Solid State Physics and Optics in Budapest (SZTEI) showed the formation of a stoichiometric compound for $x = 4$ [74]. The crystal structure was compatible with two-dimensional fullerene polymeric sheets, although the quality of the X-ray diffractogram was insufficient to determine the orientation of the polymerized molecules and the exact
bonding geometry.

An improved synthesis method developed subsequently allowed a more precise control of the stoichiometry and showed that the previously reported phase has a Mg content of $x = 5$.

We tried to gain a more precise knowledge of the crystal structure of the Mg$_3$C$_{60}$ fulleride polymer from the infrared absorption and the Raman scattering spectra. The results suggest single C$_{60}$-C$_{60}$ and Mg-C$_{60}$ bonds.

We looked for a lower limit of the depolymerization temperature by measuring the 9 GHz ESR spectrum and we found that the polymer is stable for 30 minutes at the surprisingly high temperature of 823 K. A reaction of the sample with the quartz sample holder prevented the observation of depolymerization at higher temperatures. We showed with the help of ESR and microwave conductivity measurements, that Mg$_3$C$_{60}$ is metallic at temperatures above 200 K and undergoes a gradual transition to a paramagnetic insulating state at lower temperatures [75].

5.2.2 Synthesis

Mg$_x$C$_{60}$ ($x = 0 - 6$) samples were prepared by Ferenc Borondics (SZFKI) by solid state reaction between high purity C$_{60}$ and fine Mg powder. Mg diffuses into quartz at high temperatures (700 K) so carbon steel containers were preferred for the reaction. The synthesis was performed under Ar atmosphere in a dry box to avoid unwanted reactions with oxygen. Mg grains surface was activated at 753 K and several annealing steps at temperatures from 653 K to 723 K were performed. The reaction was controlled by the solid state diffusion of magnesium in the fullerite crystallites. To improve the homogeneity of the samples the powders were reground before each annealing.

5.2.3 Crystal structure

X-ray diffraction was performed by Gábor Oszlányi (SZFKI) to determine the crystal structure of the Mg$_x$C$_{60}$ samples. The materials were found to be single-phase for $x = 3$ and $x = 5$ and $x = 5.5$. A segregation of Mg metal was observed in samples with $x > 6$.

The homogeneity of the samples was studied by HF-ESR also. As described in Sec. 3.3.2 differences in the $g$ factors split the lines of inhomogeneous phases. The spectrum of Mg$_5$C$_{60}$ consists of a single Lorentzian line at all temperatures even at the highest frequency (225 GHz). This confirms the conclusion of a single phase deduced from X-ray diffraction. The spectrum of Mg$_5$C$_{60}$ composed of several lines evidences an inhomogeneous distribution of the Mg ions and multiple phases.

For these reasons we focused our attention on the samples with Mg concentrations about five. The similarities of the diffractograms of samples with $x = 5$ and $x = 5.5$ (Fig. 5.1) indicates that Mg$_5$C$_{60}$ is not a line-phase and small deviations from the stoichiometric value of the Mg concentration do not affect significantly the crystal structure. A similar behavior was observed in the Li$_4$C$_{60}$ fulleride also [32, 76].
The X-ray diffractogramm of Mg$_5$C$_{60}$ is best fit with a concentration $x = 4$ as reported in the first paper and a rhombohedral structure with lattice parameters $a = b = 9.22$ Å, $c = 25.25$ Å and $\gamma = 120^\circ$. These values indicate two-dimensional hexagonal C$_{60}$ polymeric sheets in the $ab$ plane. The material belongs to the $R\bar{3}m$ space group. C$_{60}$ molecules are positioned at the fractional coordinates $(0,0,0)$, $(2/3,1/3,1/3)$ and $(1/3,2/3,2/3)$, while four Mg are situated at the two inequivalent positions $(0,0,0.23)$ and $(0,0,0.43)$. The position of the fifth Mg atom cannot be determined from the powder diffractograms. The difficulty in determining the exact atomic positions can be a consequence of an intrinsic disorder of the structure, (e.g. random distribution of the interfullerene bonds or variable Mg-C$_{60}$ distances).

We attempted to obtain a deeper insight of the crystal structure of Mg$_5$C$_{60}$ from the intra-molecular vibrational modes of the fullerene molecules observed by infrared spectroscopy (IR) and Raman scattering (see Sec.3.4.2). These vibrational modes are particularly sensitive to the charge state and to the distortion of the C$_{60}^-$ anions.

The IR spectrum of an isolated neutral C$_{60}$ molecule has only four active modes [4] at 526, 576, 1182 and 1428 cm$^{-1}$. Covalent bonds or the Jahn-Teller (JT) effect lower the symmetry of the molecule and new vibrational modes are activated. The large number of absorption lines in the spectrum of Mg$_5$C$_{60}$ shown in Fig. 5.2, indicates a distortion of the fullerenes by covalent bonds [77]. A Jahn-Teller distortion due to JT effect only splits the modes but does not activate many new modes. In the case of small distortions, it is possible to determine the symmetry of the molecule from the number of lines with the help of group theory. In the present case, the number of the lines is too large for the analysis. However, from comparison with the IR spectrum
of fulleride polymers in which the structure is known from other methods, a qualitative analysis of the spectrum is possible.

The absorption line around 815 cm$^{-1}$ was observed in all fulleride polymers with single bonded C$_{60}$ molecules [78, 79] as shown in Fig. 5.3. This line in the spectrum suggests that Mg$_5$C$_{60}$ contains single bonds.

The broad absorption band at 1480 cm$^{-1}$ is more difficult to assign. The extra electrons acquired by the C$_{60}$ molecules, occupy the anti-bonding $\epsilon_{1u}$ levels and inter-fullerene covalent bonds lower the number of double bonds in the molecule. Both of these effects soften the intra-molecular bonds and lower the resonance frequency of the modes. This effect is more evident for the $T_{1u}(4)$ mode. An empirical dependence of the blue-shift of its resonance frequency as a function of the anion charge state was reported [80] in fulleride salts. Based on these arguments, we conclude that the absorption line in the high frequency region of the spectrum cannot be assigned to the $T_{1u}(4)$ mode.

The nature of this mode is clarified by the analysis of the Raman spectrum. The Raman spectrum of an undistorted neutral fullerene molecule has 8 active modes. Of these modes the $A_g(2)$ around 1469 cm$^{-1}$ is the most interesting. This mode has usually the highest intensity, and similarly to the $T_{1u}(4)$ mode, is reported to down shift the frequencies with an increasing of the negative charge on the C$_{60}$ molecule.

The Raman spectrum of Mg$_5$C$_{60}$ (Fig 5.2) shows a broad feature at the same frequency than in the IR spectrum. A possible explanation is that the $A_g(2)$ mode is rendered IR active by the symmetry reduction and becomes visible in both spectra. A similar effect was reported for C$_{60}$ monolayers adsorbed on metals [81]. In these systems, the intensity of the $A_g(2)$ mode is

![Raman spectrum](image-url)
amplified by the coupling with a low-frequency vibrating mode through the interaction with a free electron gas. This effect is known in the literature as the "vibrational phase relaxation" mechanism [82].

In Mg$_5$C$_{60}$, the low frequency vibrating mode is an intermolecular mode with a frequency of about 100 cm$^{-1}$ which is observed in fulleride polymers [22, 83]. ESR and magnetic conductivity measurements presented in the next paragraph indicate delocalized electrons which couple the two vibrating modes. However, in contrast to other reported cases, the A$_s(2)$ mode is shifted about 11 cm$^{-1}$ to higher frequencies. Covalent bonds between the fullerene molecules and Mg atoms is a plausible explanation of this shift. This would result in a decrease of the electron density on C$_{60}$ with consequent strengthening of the intra-molecular carbon bonds. A small blue-shift of the A$_s(2)$ mode, as a consequence of covalent bonds, was reported in C$_{60}$ monolayers adsorbed on platinum, [84].

We made many attempts to determine the depolymerization temperature of Mg$_5$C$_{60}$ by X-ray diffraction and IR absorption at 400-500 K where all known fulleride polymers depolymerize. Only irreversible changes in the IR spectrum were observed while depolymerization of intercalated fulleride salts is expected to be reversible with temperature (see Sec. 2.3.4). These reactions were attributed to oxidation of the sample in the imperfect dynamic vacuum of the spectrometer.

Therefore, we measured a lower limit of the depolymerization temperature by searching for changes in the ambient temperature ESR spectra after annealing at higher temperatures. The Mg$_5$C$_{60}$ sample was sealed in a quartz tube under He atmosphere. It was heated at a rate of 10 K/min to each tem-
perature, kept there for 15 minutes, quenched into water and then the 9 GHz ESR spectra were recorded at ambient temperature. We repeated this cycle twice in 25 K steps between 300 and 848 K. We found that treatment up to 823 K leaves the ESR spectrum unchanged. After annealing at 848 K, the ESR spectrum and the color of the quartz sample holder changed. This indicates a reaction of Mg (diffusing out of the sample) with quartz. It is not clear whether the depolymerization would take place in absence of this reaction. We conclude that the polymer phase is stable for at least 30 minutes at 823 K.

Although many details of the structure remain elusive we concluded that there are strong indications that Mg$_5$C$_{60}$ is a two-dimensional fulleride polymer with single interfullerene bonds and it is stable up to the surprisingly high temperature of 823 K. It is plausible that one of the Mg atoms is covalently bonded to a C$_{60}$ molecule. The difficulties in determining the exact structure are associated in an intrinsic disorder of the crystal structure. Intrinsic disorder for example can arise from a bonding angle between the fullerenes which is incompatible with crystalline order or from competing mechanisms of similar importance determining the structure.

### 5.2.4 Electronic and magnetic properties

Here we present a study aimed to understand the electronic and the magnetic properties of Mg$_5$C$_{60}$ with microwave conductivity measurements and ESR at different frequencies.

The temperature dependence of the microwave conductivity of Mg$_5$C$_{60}$ is shown in Fig. 5.4. Two distinct regimes are identified. At high temperatures, the conductivity decreases with increasing temperature as in metals where the electron scattering is due to phonons. The low temperature behavior is different from usual metals. The conductivity has a broad maximum and decreases below 200 K. This behavior corresponds to a smooth transition from a metallic to an insulating state.

We determined the temperature dependence of the electron spin susceptibility from the normalized intensity of the ESR spectrum at 9 GHz and 225 GHz in the 4-300 K temperature range. For the normalization of the ESR intensity measured at $T > 100$ K, we mixed Mg$_5$C$_{60}$ with MgO doped with 1.5 ppm of Mn$^{2+}$ ions, which is a standard EPR reference. At lower temperatures the Mn:MgO ESR saturates at very low microwave power and o-KC$_{60}$ was used as reference. This fulleride polymer has a metallic ground state and a large temperature independent susceptibility down to 4 K. In metals, the spin life-time is short and the saturation of the resonance line is observed only at very high the microwave power. O-KC$_{60}$ has an ESR line width of only 0.7 mT at room temperature. All these aspects and the stability in air make this fulleride polymer an ideal ESR reference.

The temperature dependence of the spin susceptibility deduced from the ESR intensity is shown in Fig. 5.5. For both frequencies, at $T \geq 200$ K the spin susceptibility has a value of $2 \times 10^{-5}$ emu/mole and it is almost independent of temperature, as expected for the Pauli susceptibility of a degenerate electron gas. At lower temperatures, a Curie contribution which
Figure 5.4: Temperature dependence of the microwave conductivity at 10 GHz of Mg₅C₆₀. The conductivity has a smooth transition from a metal to an insulator behavior at about 200 K.

Figure 5.5: Temperature dependence of the spin susceptibility of Mg₅C₆₀ measured at 225 GHz (empty circles) and 9 GHz (squares). The two curves are normalized at 300 K. The continuous line is the Brillouin function of spin $S = 1/2$ in 8.1 T field normalized at 50 K to the 225 GHz ESR measurement.
Figure 5.6: Temperature dependence of the ESR line width of Mg$_5$C$_{60}$ measured at 9 GHz (squares) and 225 GHz (circles). The temperature dependence of the frequency independent component of the line width $a(T)$ is also shown (triangles). Note that for temperatures above 175 K, the line width at 9 GHz increases linearly with temperature as expected in metals in which the main relaxation mechanism is the electron-phonon interaction.

is characteristic of a small concentration of localized spins dominates the ESR spectrum. The transition between the two different temperature dependences is gradual and no discontinuity is observed which excludes a phase transition.

The temperature dependence of the ESR line width is shown in Fig. 5.6. The 9 GHz line is a symmetric Lorentzian with a 0.45 mT line width at room temperature and it broadens with increasing ESR frequency. The frequency and the temperature dependences of the line width can be separated into a field dependent and an independent term to give:

$$\Delta H = a(T) + b(T)H \quad , \quad (5.1)$$

The frequency independent term, $a(T)$, is almost constant below 100 K (see Fig. 5.6) and increases linearly with temperature above 100 K as in metals in which the main relaxation mechanism is the electron-phonon interaction [59]. The $b(T)$ coefficient of the field dependence increases at lower temperatures. This line broadening of $s$ suggests a slight inhomogeneity of the sample. At higher temperatures, the diffusion of the delocalized electrons “motionally narrows” the inhomogeneities by the mechanism presented in Sec. 3.3.6. The narrowing is incomplete and this explains the frequency dependence of the line width.

At 225 GHz the inhomogeneous broadening, $b(T)$, although small, hides the intrinsic phonon-induced temperature dependent broadening, $a(T)$. At low temperatures the electrons are localized. The inhomogeneities are not averaged anymore and the resonance line broadens. The broadening increases
at lower temperatures as electrons become the localized and the susceptibility of the localized electrons grows according to the Curie law.

The temperature independent susceptibility and the decreasing conductivity with temperature indicates that above 200 K M\(_g\)C\(_{60}\) is metallic. An ultimate confirmation is given by the linear increase of the 9 GHz line width with temperature indicating that electron-phonon coupling is the main relaxation mechanism.

At low temperatures, the smooth transition to an activated-like temperature dependence of the microwave conductivity and the growing of a Curie component in the susceptibility indicate a localization of the electron (and as consequence of the spins) without a transition to magnetically ordered ground state down to the lowest temperature (5 K).
5.3 The $C_{60}$-cubane copolymer $K_2C_{60}C_8H_8$

5.3.1 Previous results

A combined IR and Raman study was conducted to determine the isomeric form of the cubane molecules in the polymeric structure [85]. The authors suggested from symmetry considerations that the most probable is dihydropentalen, a planar molecule. They also showed that interfullerene bonds are absent and confirmed the copolymeric nature of the structure. A study of the fullerene-cubane phase diagram at high temperatures (up to 800 K) and pressures (some GPa) showed different copolymeric structures [86].

Similarly to fullerene photopolymers these polymers are insulating, with all the electrons localized in covalent bonds. As seen in Chapter 2, the properties of fullerenes can be modified by alkali intercalation. This motivated us to intercalate the copolymer with potassium and to study the properties of the resulting alkali-fulleride-cubane copolymer, $K_2C_{60}C_8H_8$. Intercalation of the cubic rotor-stator phase directly was not possible as the solid state reaction is inefficient below the polymerization temperature.

We find from microwave conductivity, ESR and SQUID magnetometry that the pristine material is insulating while $K_2C_{60}C_8H_8$ is metallic at $T > 200$ K. At lower temperatures, localization of the electrons leads to an insulating ground state similar to that observed in Mg$_5$C$_{60}$.

5.3.2 Synthesis

The rotor-stator monomeric material $C_{60}C_8H_8$ was prepared from toluene solutions of fullerenes and cubane by evaporating the solvent [35]. The crystallite sizes were 5-200 $\mu$m. A 36 hours long heat treatment was performed at 473 K to polymerize the sample.

Poly($C_{60}C_8H_8$) was then reacted with stoichiometric amount of K in a steel vessel heated inside a dry box. The reaction mixture was heated at 523 K for 2 weeks with one intermediate regrinding for homogenization.

5.3.3 Crystal structure

The resulting intercalated material was characterized by Infrared (IR) spectroscopy and X-ray diffraction. The absorption line of pure $C_{60}$ and pure cubane in the infrared spectrum of the monomeric material $C_{60}C_8H_8$ confirmed the Van-der-Waals nature of the bonds between the two molecules [35]. In the polymerized poly($C_{60}C_8H_8$) material many absorption modes are a consequence of the lowering of the symmetry by covalent bonds. In this spectrum the $T_{1u}$ modes of the $C_{60}$ molecule are still recognizable. The $T_{1u}(4)$ mode, the most sensitive to the charge state, is also split due the lowering of the symmetry with the main component at 1424 cm$^{-1}$[85].

In $K_2C_{60}C_8H_8$, this peak is found at 1362 cm$^{-1}$, indicating a charge transfer from the K atoms to the $C_{60}$'s [77, 87]. The exact amount of the charge transfer cannot be determined because in covalent bonded structures the
empirical relations between the charge state of the anions and the resonance frequency of the vibrating mode is no longer valid.

![Figure 5.7: X-ray diffraction pattern of K₂C₆₀C₈H₈. The absence of peaks in the high angle diffraction region indicate a strong disorder in the crystalline structure.](image)

X-ray diffraction showed a high degree of disorder. The highest angle at which a diffraction peak can be observed is an indication of the crystalline order of a sample. The diffraction peaks at high angles arise from rapid spatial variations of the electronic density in the sample. The highest is the angle the highest is the spatial resolution of the diffraction pattern. A shown in Fig. 5.7 the last reflection is observed at 35 degree which corresponds to a spatial resolution of 2.56 Å. For ordered crystals this value is lower than 1 Å. This indicates that the electronic density distribution in the sample is smeared by the disorder of the atomic positions.

The diffraction pattern at small angles can be well described with the face centered cubic structure of the monomeric C₆₀·C₈H₈ and shows that the K⁺ ions occupy the sites related to the tetrahedral ones in the pristine cubic rotor-stator material.

### 5.3.4 Electronic and magnetic properties

We first treat the electric and magnetic properties of the pristine fullerenecubane copolymer as a reference material. The absence of measurable losses in poly(C₆₀C₈H₈) powder in the microwave cavity indicates that the conductivity of the sample is low. The Curie-like temperature dependence of the spin susceptibility obtained from the intensity of the ESR spectrum confirms that this polymer is an insulator. ESR absorption intensity corresponds to a concentration of about 0.5 percent per C₆₀ molecule assuming $S = 1/2$ spins.
These paramagnetic centers are localized defects in the polymeric structure. The full width at half maximum (FWHM) line width is mainly due to the dipole-dipole interaction as confirmed by the nearly temperature independent value of 0.15 mT (see Fig. 5.8). This value is in good agreement with the 0.2 mT calculated from the Van Vleck formula (see Sec. 3.3.4) for spins localized on the $C_{60}$ molecules.

![Graph](image)

Figure 5.8: Temperature dependence of the 9 GHz ESR line width of pristine poly($C_{60}$C$_8$H$_8$) (circles) and K$_2$C$_{60}$C$_8$H$_8$ (squares) polymers.

Potassium intercalation drastically changes the microwave conductivity of the polymer $\sigma(T)$. As shown in Fig. 5.9, $\sigma(T)$ is characterized by a broad maximum at about 400 K. At higher temperatures, the conductivity decreases linearly with $T$ as in metals in which the electron-phonon coupling is the main relaxation mechanism. At lower temperatures, the behavior is activated-like. At $T<250$ K, the conductivity of the sample is too low to induce measurable losses indicating a transition to an insulating ground state.

The two orders of magnitude higher intensity of the ESR signal confirms the charge transfer from K to the $C_{60}$ molecules. The contribution to the overall signal of the defect in the polymeric structure can be neglected in the intercalated material.

Similar to Mg$_5$C$_{60}$, we obtain the static susceptibility from the integrated intensity of the ESR spectrum for $T > 130$ K and in the whole temperature range by SQUID magnetometry. The absolute values shown in Fig. 5.10, obtained by the two different techniques agree within experimental accuracy in the common temperature range.

The Pauli contribution to the susceptibility, $\chi_P = 8 \times 10^{-4}$ emu/mole is large. It is comparable to that of orthorhombic KC$_{60}$ [44] and cubic K$_3$C$_{60}$
Figure 5.9: Temperature dependence of the microwave conductivity, $\sigma(T)$, of $K_2C_{60}C_8H_8$ normalized to the room temperature value. About 400 K the conductivity changes smoothly from metallic to activated-like.

[6]. In a free electron model, the measured susceptibility would correspond to a Fermi temperature, $T_F$ of 400 K only.

The Pauli formula is the first term of the expansion in series of the magnetic susceptibility of a free electron gas as a function of the $(T/T_F)$ ratio, where $T$ is the temperature of the electron gas. When $T$ is comparable to the Fermi temperature the following temperature depending terms of the series have to be taken into account as well. Thus, according to the free-electron model the susceptibility of $K_2C_{60}C_8H_8$ polymer would be temperature dependent in contrast to the temperature independent observed value.

This contradiction indicates that the electron-electron correlations are relevant in this material. The Coulomb interaction enhances significantly the susceptibility with the mechanism described in Sec.3.3.2.

Below 40 K, the susceptibility rises rapidly with decreasing temperature. At the lowest temperatures, it corresponds to about 10 percent of $C_{60}$ having an $S = 1/2$ spin.

The 9 GHz ESR line width increases with temperature from 0.05 mT at 100 K to 0.18 mT at 350 K (Fig. 5.8). At temperatures higher than 300 K, the increase is linear with $T$ as in metals in which the main spin relaxation mechanism is due to the electron-phonon coupling [59]. For $T < 320$ K, the line width is smaller than in the pristine polymer. The dipole-dipole interaction effective in the pristine polymer is narrowed in the intercalated material by the diffusion of the conducting electrons.
Figure 5.10: Temperature dependence of the spin susceptibility of K$_2$C$_{60}$C$_8$H$_8$ measured by SQUID (squares) and 9 GHz ESR (circles).

The 225 GHz ESR spectrum of K$_2$C$_{60}$C$_8$H$_8$, shown in Fig. 5.11, is a characteristic three-axes $g$-factor anisotropy powder spectrum (see Sec. 3.3.3) with three singularities ($g_1 = 2.00464$, $g_2 = 2.00462$, $g_3 = 2.0044$) at all temperatures. The narrowness of the intrinsic line width excludes that the material consists of segregated phases observed in KC$_{60}$ and Na$_2$C$_{60}$. The presence of more phases would split or inhomogeneously broaden the high frequency ESR absorption line.

The $g$-factor anisotropy indicates the presence of well defined crystallites with dimensions comparable to the spin diffusion length, typically 200 nm in conducting fullerenes [6].

Remarkably, the powder spectra is observed also in the metallic temperature range. This is unusual, because generally the anisotropy is smeared out by the diffusion of the electrons. A possible explanation is that the anisotropy is not intrinsic but depends from the morphology of the sample. If the crystallites grow preferentially with well defined relative orientations and the electronic diffusion between them is negligible, the resulting structure is anisotropic with an external applied magnetic field. The effect is small and this is the reason why it is not detectable by X-ray diffraction which finds the crystalline structure cubic.

The growing of the Curie component of the susceptibility between 40 and 5 K is accompanied by an increase of the intrinsic line width extracted from the fit of the 225 GHz ESR powder spectra from 0.35 mT to 0.55 mT (Fig 5.12). In the case of K$_2$C$_{60}$C$_8$H$_8$ the broadening is faster and may be a signature of growing antiferromagnetic interactions between the localized
Figure 5.11: 225 GHz ESR spectrum of $\text{K}_2\text{C}_{60}\text{C}_8\text{H}_8$ measured at 120 K. The fit assumes a three axis $g$-factor anisotropy with $g_1$, $g_2$, $g_3$ given in the text.

Figure 5.12: Temperature dependence of the 225 GHz ESR line width. Note the line broadening at temperatures below about 40 K.
spins without the transition to a magnetically ordered ground state at the lowest temperature reached (5 K).

In an antiferromagnetic state, there is a preferential direction along which the spins are oriented (the easy axis) and the sample is anisotropic with respect to an applied magnetic field. In powder samples, crystallites with all possible orientations broaden the absorption line.

In conclusion, K$_2$C$_{60}$C$_8$H$_8$ is metallic at high temperatures according to both microwave conductivity measurements and ESR. However, spin susceptibility and conductivity are metal-like in different temperature ranges: the susceptibility is Pauli-like at $T > 200$ K and the conductivity decreases linearly with temperature for $T > 400$ K. We attribute this difference to the sensitivity of conductivity to morphology and disorder. In sample consisting of by small metallic domains in an insulating matrix. The conductivity is dominated by the isolating matrix which prevents flow of currents while the magnetic susceptibility is metallic.

5.4 Discussion

Both fulleride polymers (M$_{55}$C$_{60}$ and K$_2$C$_{60}$C$_8$H$_8$) are metallic above a certain temperature and show a smooth transition to an insulating ground state upon lowering $T$. In M$_{55}$C$_{60}$, the transition is in the same temperature range in the magnetic susceptibility and the conductivity. A 200 K difference is observed in K$_2$C$_{60}$C$_8$H$_8$. This difference can be attributed to a larger inhomogeneity of the copolymeric material, e.g. due to imperfect intercalation, which influences prevalently the conductivity. In K$_2$C$_{60}$C$_8$H$_8$, electron-electron correlations are more important as shown by the large value of the susceptibility and the possible antiferromagnetic correlations below 40 K.

Apart from these differences, conclusions valid for both materials can be done. Both material are single-phase and only slight inhomogeneities were observed. Structural changes that could cause the electron localisation was not detected by the various experimental methods.

The change of the temperature dependence of the static susceptibility from Pauli to Curie-like is gradual and there is no well-defined phase transition. We do not observe a Mott-Hubbard transition which usually has a well defined transition temperature and results in a magnetically ordered ground state.

The gradual transition from metallic to insulating behavior cannot be ascribed to the development of a spin gap at low temperatures. In that case the contribution of the conducting electrons to the magnetization would decrease exponentially with the lowering of the temperature in the range of $E_g/k_B$ where $E_g$ is the value of the gap and $k_B$ is the Boltzmann constant. Instead, the decrease of the conductivity with temperature is accompanied by an increase of the spin magnetization down to the lowest temperature (5 K) in both polymers.

The disorder of the crystal structure showed by the X-ray studies suggests a possible explanation. The disorder in the atomic position results in a random spatial distribution of the potential wells seen by the electrons.
Metallic disordered fulleride polymers

The problem of an electron diffusing in a random potential was first treated by P.W. Anderson [88]. He demonstrated that when the range of the values of the potential wells, $V_0$ becomes comparable with the band-width the electronic states become localized. Mott [89] pointed out that even when the ratio $V_0/W$ is smaller than the critical value, the states in the band tails below a certain energy value called "mobility edge" become localized. Increasing disorder, increases the value of the mobility edge. If the Fermi energy lies below $E_c$ the ground state is insulating. Electrons are excited over the mobility edge at temperatures much higher than $E_c/k_B$ and behavior is metallic.

In the present cases, electron-electron correlations, structural disorder and dimensionality play a role in the electronic localization. The theoretical description of a strongly correlated electron gas in a disordered lattice is a challenging not a solved problem although recently important results have been reported [90, 91]. Moreover, the high temperature at which localization is observed indicates that the scaling theory [92] obtained in the weak localization limit cannot be applied.

To our knowledge, Anderson localization has not been observed experimentally in fulleride materials. Theoretically, Gunnarsson investigated the possibility of Anderson metal-insulator transition induced by the disorder caused by phonons [6]. He calculated the temperature dependence of the resistivity by taking into account the electron-phonon couplings using a Quantum Montecarlo simulation method and found no localization. We note here that in Mg$_3$C$_{60}$ and K$_2$C$_{60}$C$_8$H$_8$, the disorder is not phonon-induced but structural, differently from the case analyzed by Gunnarsson.

In conclusion, we explain the low temperature behavior of the conductivity of the two polymers as the activation of the electrons above the mobility edge. At temperatures well above the maximum, we measured the conductivity of a metal. The description of the behavior near the maximum, where the two contributions are comparable, requires a deeper knowledge of the disorder-potential and of the phonon structure.
Chapter 6

The Li$_4$C$_{60}$ fulleride polymer

6.1 Introduction

In this chapter we present the structural, electronic and magnetic properties of the Li$_4$C$_{60}$ fulleride. $^7$Li NMR and frequency dependent conductivity measurements performed at the University of Parma (IT) by the group of Mauro Riccò on polymeric Li$_4$C$_{60}$ shows that this material is a good ionic conductor. \textit{Ab initio} theoretical calculations of the crystal structure performed by Gábor Csányi at the University of Cambridge (UK) supports these findings. These results are quite remarkable since it is the first time that ionic conductivity is observed in a fulleride material. The Li$^+$ ion dynamics strongly influences the electronic configuration of the paramagnetic centers of the polymeric structure as shown by our HF-ESR and microwave conductivity measurements.

The chapter is divided into two parts. In the first part, the main properties of the polymeric phase will be presented. The second deals with the depolymerization and the properties of the high temperature monomeric phase.

6.2 The polymeric phase

6.2.1 Crystal structure

An early study published in 2001 reported the first indications of a polymeric phase in Li$_4$C$_{60}$ [31], later the correct crystal structure was determined by Margadonna \textit{et al.} in 2004 [93, 32]. As anticipated in Sec. 2.3.4, in Li$_4$C$_{60}$ both single and double bonds connect the fullerene molecules (Fig. 6.1). The structure can be derived from the \textit{fcc} lattice of the pristine fullerite. As in KC$_{60}$, double bonds form along the face diagonal where the interfullerene distance is the shortest. The cycloaduct bonds shorten the interfullerene distance and distort the cell from cubic to orthorhombic. In Li$_4$C$_{60}$ single bonds interconnect the polymeric chains and the final symmetry of the cell is body center monoclinic (space group I2/m). The interfullerene distance is about 9.05 Å along the (2+2) cycloadducted chain (\textit{b} direction) and is somewhat larger, 9.33 Å along the single bonds (\textit{a} direction). The distance between the polymeric planes is 15.03 Å.
Figure 6.1: Representation of the Li$_4$C$_{60}$ polymeric sheets in two different renderings. The two figures have the same orientation. In the three dimensional rendering, [94], the Li$^+$ sitting in the pseudo-tetrahedral (red spheres) and in the pseudo-octahedral sites (green spheres) are also indicated. The yellow circle indicates a pseudo-octahedral site.

Although the unit cell is no more face centered cubic, it is still possible to define the interstitial sites with respect to the tetrahedral and octahedral sites of the undistorted cell. These sites will be named in the following as pseudo-tetrahedral (p-T) and pseudo-octahedral (p-O).

The X-ray diffraction pattern shows that two Li$^+$ ions are sitting in the larger p-O site in symmetry equivalent positions and the remaining two are in the p-T sites. As seen in Sec. 2.3.2, the p-T interstitial sites can accommodate more than one Li$^+$ in contrast to the tetrahedral sites.

Ab initio calculations of the crystal structure of stoichiometric Li$_4$C$_{60}$ by G. Csányi used the Cambridge CASTEP plane-wave density functional theory (pw-DFT) code described in [95]. The calculated optimized structure confirmed the X-ray diffraction results with the exception of the position of the cations in the p-O site. As shown in Fig. 6.2, the calculated positions are slightly shifted along the a direction respect to the experimentally observed ones. Interestingly, this configuration is characterized by two new Li$^+$ interstitial positions in the p-O site, at the corners of an imaginary rectangle in the ac plane.

The energy of configurations with different p-O fillings with respect to the optimized structure were also computed. In particular, the two different configurations (one p-O site is triply occupied and one is only single occupied) have an extra energy of 0.47 and 0.35 eV only with respect to the doubly occupied configuration. The configuration in which one p-O site is quadruply occupied and two others contain one Li$^+$ has an energy of 1.04 eV.

In the stoichiometric polymeric Li$_4$C$_{60}$ there are unoccupied interstitial p-O sites that can be filled by Li$^+$ cations. Configurations in which more than two cations occupy the p-O site have low energies and can form at low temperatures. The free sites in the structure allow Li$^+$ diffusion in the lattice. Li$^+$ cations can move along crystalline directions with alternating
The $Li_4C_{60}$ fulleride polymer

Figure 6.2: Schematic representation of the pseudotetrahedral site. Left: Section of the ideal tetrahedral site in the $ac$ plane. Right: Same section of the distorted octahedral site after polymerization along the $a$ direction. Green circles indicate the $Li^+$ position according to X-ray diffraction. The yellow circles indicate positions suggested by the calculation.

the $p$-$T$ and the $p$-$O$ sites. The aperture connecting the tetrahedral and the octahedral sites is small and allows the diffusion of small ions only. This steric effect prevents ionic diffusion at low temperatures in other alkali intercalated fulleride salts. The cationic radius of $Li^+$ is small and it is reasonable to assume lower energy barriers between the different sites in contrast to larger alkali atoms.

Figure 6.3: Three-dimensional rendering of a doubly (1) and triply (2-3) occupied $p$-$O$ site from the $ab$ initio calculations. Configuration (2) has an energy of 0.47 eV (3) of 0.35 eV with respect to (1). The rectangle is the same as in Fig. 6.2 and is only a guide to the eye.

6.2.2 $Li^+$ dynamics

Nuclear magnetic resonance (NMR) performed on $^7Li$ nuclei is a major tool to probe the dynamic behavior of the $Li^+$ cations. The NMR spectrum is narrowed by the relative motion of the nuclei with respect to the surrounding if $\Delta \omega \tau \ll 1$. Here $\Delta \omega$ is the line width and $\tau$ is the correlation time which describes the motion of the nuclei. The mechanism is equivalent to those presented in Sec. 3.3.6 for the ESR absorption line.

At low temperatures, the line is a quadrupolar powder spectrum [54]. The line width decreases with increasing temperature and at room temperature the spectrum is composed of a single narrow peak. The narrowing of the line is more evident above 200 K and suggests an activation of the $^7Li$ nuclei
motion [97]. The spin lattice relaxation rate T_1 is well described by a single exponential decay.

In Fig. 6.4 the temperature dependence of the $^7$Li spin lattice relaxation rate 1/T_1 measured at two different applied magnetic fields (2 and 5 T) is shown [96]. At these fields the spin relaxation rate T_1 has a peak due to the Li$^+$ motion when $\omega T = 1$. This allows a measurement of the relaxation time at the temperature of the peak. The values of the relaxation times are $\tau(323K) = 4.80$ ns and $\tau(352K) = 1.92$ ns. A detailed analysis of the temperature dependence of the spin lattice relaxation times in the framework of the Bloembergen-Purcell-Pound (BPP) theory [98] allowed to determine the temperature dependence of the correlation time which describes the Li$^+$ motion: $\tau = \tau_0 \cdot e^{E_a/k_B T}$ with $\tau_0 = 2.4$ ps and an activation energy $E_a = 190$ meV [96].

In conclusion, NMR measurements indicate the activation of Li$^+$ motion at temperatures above 200 K. The ion dynamics is well described by a single correlation time which depends exponentially on the temperature.

### 6.2.3 Ionic conductivity

The dynamics of the Li$^+$ cations showed by NMR in addition to its insulating ground state suggested that polymeric Li$_4$C$_{60}$ is an ionic conductor. To verify this supposition the temperature and frequency dependence of the conductivity were studied [96].

The experiments were performed under inert atmosphere in a dry box on pellets of polymeric Li$_4$C$_{60}$ contacted with silver paint. DC conductivity was measured inverting the polarization of the current every 200 msec in order to avoid Li$^+$ accumulation at the electrodes. An activated behavior
Figure 6.5: Up: frequency dependence of the imaginary part of the impedance $Z''$ of polymeric Li$_4$C$_{60}$. The continuous line is a fit to a Debye model. Down: Cole-Cole representation of the real and imaginary parts of the impedance [96].

is observed at temperatures above 125 K that is well described by a single exponential activation law. The activation energy of 209 meV is in good agreement with the value found by NMR measurements for the Li$^+$ motion. The large conductivity at 300 K ($\approx 10^{-2}$ S/cm) indicates the absence of Schottky barriers at the electric contacts and confirms the intrinsic nature of the temperature dependence.

The proof of the ionic nature of the conductivity is given by the frequency dependent impedance measurements. For frequencies well below the plasma edge the electronic conductivity is frequency independent. In ionic conductors the mass of the ions is much higher and the relaxation effects appear at
lower frequencies.

The response of a material to an alternating voltage can be described by an equivalent electric circuit of resistances and capacitances. The simplest case is an RC circuit with a resistance $R$ and a capacitance $C = \varepsilon_0 \varepsilon'$ in parallel. Here $\varepsilon'$ is the real part of the dielectric constant that for an ionic conductor is described by the Debye model. In this model, the relaxation of the polarization $P(t)$ induced by the applied electric field decays as a single exponential:

$$\frac{\partial P}{\partial t} = \frac{1}{\tau} (P(t) - \chi_0 E(t)) \quad ,$$

where $\tau$ is the relaxation time and $\chi_0$ the static electrical susceptibility of the material in an electric field $E(t)$. Fourier transforming this expression and using the relations: $P(\omega) = \varepsilon_0 \chi(\omega) E(\omega)$ and $\varepsilon = \varepsilon_0 (1 + \chi(\omega))$, the following expression is found for the dielectric constant:

$$\varepsilon = \varepsilon_0 + \frac{\chi_0}{1 + i \omega \tau} \quad ,$$

The frequency dependent impedance of polymeric Li$_4$C$_{60}$ is shown in Fig. 6.5. Remarkably, $Z''$ as a function of $Z'$ is a perfect semicircle as expected for an ideal RC circuit confirming the absence of other resistances and capacitances in series from the electric contacts.

In the upper panel of Fig. 6.5 the imaginary part of the impedance $Z''$, which is directly proportional to $\varepsilon'$, is shown as a function of frequency. At all temperatures, $Z''$ increases with increasing frequency to a maximum after which it begins to decrease as expected for a Debye solid. The maximum corresponds to the loss peak and is observed at the angular frequency $\omega$ at which $\omega \tau = 1$. It was possible to determine the activation energy and the correlation time. The activation energy is about 209 meV in good agreement with NMR. In contrast, $\tau_0$ was found to be 60 times higher (119 ps). This discrepancy suggests a diffusion mechanism characterized by several correlation times. However, the complete description of the Li$^+$ dynamics is still unknown and requires further studies.

### 6.2.4 Electronic conductivity

For temperatures below 250 K, the microwave losses in the cavity from the sample are very small confirming the insulating nature of this phase [32]. At higher temperatures the microwave conductivity of the polymeric phase is anomalous, there is a maximum at 300 K (Fig. 6.6).

To gain further insight into the nature of the electronic state of this phase we studied the high frequency ESR spectrum. It was shown previously [97], that the polymeric phase of Li$_4$C$_{60}$ has paramagnetic centers in a concentration of about 1 percent per C$_{60}$ molecules attributed to defects of the crystal structure. The spin susceptibility measured by 9 GHz ESR [97] shows an interesting temperature dependence. For temperatures below 100 K the behavior is Curie-like. Above this temperature the susceptibility
Figure 6.6: Temperature dependence of the microwave conductivity of polymeric \( \text{Li}_4\text{C}_{60} \) normalized to one at 295 K.

is approximately constant to about 250 K where it starts to increase with \( T \). At 450 K the susceptibility is four times larger than at 250 K.

In Fig. 6.7, the temperature evolution of the HF-ESR spectrum of polymeric \( \text{Li}_4\text{C}_{60} \) is shown. Between 150 K and 280 K the spectrum is the sum of two components. One is an isotropic Lorentzian line while the other is a powder spectrum with an uniaxial \( g \)-factor anisotropy. In the following, we will refer to these two lines as the isotropic and the anisotropic components of the spectrum.

Interestingly, the \( g \)-factor anisotropy increases with the lowering of the temperature from 0.3 mT at 290 K to 0.6 mT at 160 K. The intensity of the isotropic component of the spectrum divided by the total intensity \( I_\text{iso}/I_\text{tot} \), is strongly temperature dependent and is shown in Fig. 6.8. At \( T > 260 \) K the isotropic component dominates the spectrum, while in the 220-260 K range the above ratio increases and reaches a constant value near 160 K where the anisotropic component is the most important. For \( T < 150 \) K, the saturation of the ESR lines prevented further measurements. The position of the isotropic component coincides with the first moment of the anisotropic one in the full temperature range.

We interpret this temperature dependence of the ESR spectrum as a consequence of the hopping of localized electronic states activated for \( T > 150 \) K. At low temperatures, the major part of the localized electronic states diffuse slowly with respect to the ESR time scale. The electrons which are seen static by ESR give an uniaxial \( g \)-factor anisotropy absorption line due to the low symmetry of the surrounding. The electrons which diffuse rapidly average the anisotropy and give the isotropic component of the spectrum.

Two distinct effects influence the ESR spectrum at higher temperatures. First, the fraction of the rapidly diffusing electrons and so the intensity of the
Figure 6.7: Temperature evolution of the 222.4 GHz ESR spectrum of polymeric Li$_4$C$_{60}$. A simulation is shown below each spectrum. At the two lowest temperatures the spectrum is fitted with an uniaxial $g$ factor powder spectrum and a Lorentzian line. The spectrum at 340 K is the sum of a three-axial $g$ factor powder spectrum and a Lorentzian line.

isotropic component increases. Second, the slowly diffusing electrons spend more time in a more isotropic environment giving a temperature dependent $g$-factor anisotropy. According to the ESR, 90 percent of the electrons are rapidly diffusing at 280 K. This mechanism differs from the classical "mo-
tional narrowing\(^n\) of the absorption line where no changes in the \(g\)-factor with increasing temperature is expected [54].

The motion rate \(1/\tau\) of the hopping electrons can be estimate with the expression for the motional narrowing given in Sec. 3.3.6: \(\Delta \omega(T) = (\Delta \omega(0))^2 \cdot \tau\). \(\Delta \omega(0)\) and \(\Delta \omega(T)\) are the width of the static and the narrowed ESR spectrum respectively. The width of the static spectrum is about equal to the \(g\)-factor anisotropy measured at the lowest temperature, 0.45 mT at 150 K. The line width of the isotropic component is equal to 0.07 mT at 300 K. These values can be expressed in GHz by multiplying for the gyromagnetic ratio of the free electron \(\gamma = 28\) GHz/T. The motion rate at 300 K is then about 1 GHz, a very low value for an electron in a crystal.

It is important to observe here that the fast diffusing electrons are not delocalized. If they were delocalized they would give a common ESR resonance line with the "static" electrons and the two components of the spectrum would not be distinguishable.

![Figure 6.8: Temperature dependence of the intensity of the homogeneous component of the 222.4 GHz ESR spectrum respect to the overall intensity. At 275 K the 90 percent of the ESR intensity is in the homogeneous component.](image)

This increase of the number of hopping electrons explains the increase with temperature of the microwave conductivity below 300 K. Interestingly, the motion of the localized electronic states sets on in the same temperature range as the \(\text{Li}^+\) diffusion is shown by \(^7\text{Li}\) NMR. This suggests that static \(\text{Li}^+\) ions bind the electrons.

At about 290 K the ESR spectrum gradually changes. New paramagnetic centers with a rhombic \(g\)-factor anisotropy appear (Fig. 6.7). The intensity of this component is about a third of the isotropic one at 340 K. The spectrum
The $Li_4C_{60}$ fulleride polymer broadens with lowering temperature due the increase of the intrinsic line width and of the $g$-factor anisotropy. This prevents to determine whatever this spectral contribution is present at all temperatures or appears at about 275 K.

In conclusion, HF-ESR observes slowly hopping localized electronic states that contribute to the microwave conductivity of the polymeric phase of $Li_4C_{60}$. We suggest that the electronic states are small-polarons [62, 99].

One of the first descriptions of polarons was given by Holstein [100]. He described an electron moving slowly with respect to the phonon frequency in an insulating material. The electron-phonon interaction is usually small and can be treated as a perturbation of the electronic states. In this case the interaction gives rise to electronic transitions and limits the life-time of the electrons. For large values of the electron-phonon coupling constant the interaction cannot be treated as a perturbation and changes the electronic configuration.

The strong electron-phonon interaction distorts and polarizes the lattice near the electron. This distortion results in an excitation of the phonons and provides a potential well for the electron which becomes localized. The polaron is the quasi particle constituted by the self-trapped electron and the coupled phonon cloud. The polaron is called "small" when the electron localization length is comparable to the lattice constant.

Small polarons can move in the lattice leaving the number of excited optical phonons unchanged or by changing it. The first process called "diagonal" is dominant well below the Debye temperature and gives rise to Bloch-like energy bands. The non-diagonal transitions in this temperature limit the life time of the polaron. With increasing temperature the probability of the non-diagonal transitions increases and the life-time of the polaron becomes comparable to the band width. At these temperatures the motion becomes hopping-like.

The effect of non-interacting polaron motion on conductivity was also studied by Holstein [100]. He found a decreasing conductivity with temperature in the band-regime and an activated conductivity in the hopping regime. A model of correlated small polaron motion was suggested by Ihle and Lorenz [101, 102] to describe the conductivity of $Fe_3O_4$. They showed that polaron-polaron correlations change the temperature dependence of the conductivity. In the band regime, a gap in the small-polaronic band opens resulting in an activated behavior of the conductivity in contrast to the non-interacting case. The authors explain the maximum in the dc conductivity observed for this material as a crossover between the two possible conduction mechanisms, band-like and hopping-like, of interacting polarons.

In $Li_4C_{60}$ the small polaron concentration is low and polaron-polaron interactions can be neglected. However, polarons bind to the $Li^+$ atoms at low temperatures according to ESR. This suggests a correlation between the small polarons and the ions motion. We suggest that this correlation could give rise to the observed maximum in the conductivity at room temperature with a similar mechanisms as that $Fe_3O_4$.

The decrease of the conductivity could be a consequence of structural
changes, e.g. defects of the polymeric sheets as suggested by the increasing spin susceptibility for \( T > 275 \). The susceptibility increases by a factor of four between 250 K and 450 K. Thus the concentration of magnetic defects would increase by about a factor of 7.2 according to the Curie law. Although, X-ray diffraction does not observe important changes in the crystal structure [97] these cannot be excluded since this experimental method has a limited sensitivity. Structural changes usually show hysteresis cycles with temperature that are not observed by microwave conductivity measurements.

At this stage of the studies is not possible to determine the exact mechanism of the polaronic conduction in \( \text{Li}_4\text{C}_{60} \) and further structural studies are required to understand the temperature dependence of the microwave conductivity in this temperature range. It is important to stress that the concentration of mobile electrons is small and small-polaron conduction in \( \text{Li}_4\text{C}_{60} \) contributes significantly to the conductivity at frequencies higher than the loss peak only, where the ionic contribution is no more important. For this reason at microwave frequencies the conductivity of the sample is determined by the electronic (polaronic) conduction.

### 6.3 Depolymerization and monomeric phase

At temperatures above 470 K, X-ray diffraction observes a monomeric phase which coexists in a wide temperature range with the polymeric phase as shown in Fig. 6.9. Depolymerization is complete at about 600 K. A large hysteresis is observed on cooling.

![Figure 6.9: Depolymerization of \( \text{Li}_4\text{C}_{60} \) followed by X-ray diffraction. The polymeric and monomeric phases coexist in a large temperature range [97].](image)

The effect of depolymerization on the temperature dependence of the microwave conductivity \( \sigma \) is shown in Fig. 6.10. Different \( \sigma(T) \) curves were measured by heating from 200 K to 350, 600 and 690 K and cooling down at
the same rate of 8 K/minutes. Below 200 K, the conductivity was too small to induce measurable microwave losses. All \(\sigma(T)\) curves show an increase with increasing temperature from 200 K and have a maximum around 300 K as seen in the previous paragraph. At higher temperatures, the conductivity decreases to a minimum at 410 K after which it increases rapidly. At 690 K, the conductivity of Li\(_4\)C\(_{60}\) is about 20 times larger than at room temperature. Hysteretic behavior is observed above 420 K. A second \(\sigma(T)\) curve measured up to 690 K showed a smaller hysteresis loop and a shift in the minimum of the conductivity from 420 K to 380 K.

![Graph](image)

Figure 6.10: Depolymerization of Li\(_4\)C\(_{60}\) followed by microwave conductivity measurements. The curves were obtained heating the sample to 600 K (red squares), 690 K a first time (blue triangles) and a second time (green circles). The arrows indicate the sign of the temperature sweep. At temperatures above 450 K Li\(_4\)C\(_{60}\) depolymerizes and the conductivity increases as the metallic monomeric phase forms.

The increasing \(\sigma\) with increasing \(T\) in the temperature range where Li\(_4\)C\(_{60}\) monomer domains grow is explained by assuming that the high temperature monomeric phase is a good conductor. This is in agreement with previously reported ESR and NMR results [103]. The room temperature sample conductivity is unaffected by thermal cycling however the hysteretic loop of the second thermal cycle is smaller. These observations indicate that the polymer morphology has a thermal history dependence but does not influence the overall electronic properties.
Chapter 7

Theses

1. I took part in the project to modernize the high frequency electron spin resonance (HF-ESR) spectrometer at the Budapest University of Technology and Economics. I constructed the probe head and the vibration isolated supporting structure of the spectrometer. The self resonant frequency of the structure is 10 Hz and this low value guarantees the mechanical stability needed to measure small intensity ESR signals. The sensitivity of the upgraded spectrometer, about $10^{10}$ spin/G at 222.4 GHz, is comparable to the best 9 GHz commercial spectrometers.

2. I measured the various phase transition temperatures of the KC$_{60}$ fulleride with HF-ESR and microwave conductivity. I demonstrated that these experimental techniques are particularly suitable to evidence phase segregations in fullerides. The enhanced spectral resolution of the high frequency ESR allows to separate the contributions of phases with slightly different $g$ factors which have a common line in commercial 9 GHz ESR spectrometers. The contactless microwave loss measurements allow for a precise measurement of the intrinsic electric conductivity.

3. My high frequency ESR measurements evidence phase segregation on a nanoscale in the Na$_2$C$_{60}$ fulleride salts below 450 K. The spin susceptibility extracted from the ESR intensity demonstrates that at least one of these phases is metallic. I showed that at higher temperatures the Na$^+$ ions diffuse and the material is homogeneous with a stoichiometric composition of Na$_2$C$_{60}$ at 520 K. I confirmed the role of the Na$^+$ ion diffusion in the segregation process with HF-ESR measurements on samples quenched from temperatures above 520 K.

4. I showed with multifrequency ESR that the fulleride polymer Mg$_5$C$_{60}$ is a homogeneous material, stable to at least 823 K. I performed infrared and Raman studies that suggest single bonds between the fulleride ions and possible Mg-C$_{60}$ covalent bonds. In a combined ESR and microwave conductivity study, I showed that Mg$_5$C$_{60}$ is metallic above 200 K and undergoes a gradual transition to a paramagnetic insulating state at lower temperatures. I attributed this transition to Anderson
localisation of the electronic states driven by the intrinsic disorder of the crystal structure. From a study of the ESR line width I suggested that the main spin relaxation mechanism is the electron-phonon coupling.

5. I studied by microwave conductivity and ESR the effect of potassium intercalation on the electric and magnetic properties of poly(C_{60}C_8H_8). I showed that the resulting K_2C_{60}C_8H_8 copolymer is metallic at T > 200 K, in contrast to the pristine poly(C_{60}C_8H_8) copolymer that is an insulator at all temperatures. At lower temperatures K_2C_{60}C_8H_8 has a gradual transition to a magnetic insulator ground state that I attributed to a disorder-driven Anderson localization of the electronic states.

6. I showed that hopping localized electronic states contribute to the microwave conductivity of the polymeric phase of the Li_4C_{60} fulleride. I studied the effects of depolymerization on the microwave conductivity and showed that the monomer phase is a good conductor.

Publications related to my Ph.D. work:


Further publications:


Chapter 8

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Bibliography


