Solid State and Magnetic Properties of Pure, Intercalated and Superconducting Fullerenes

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Abstract
A review of some of the solid state and the magnetic properties of fullerenes is presented. We summarise and discuss experimental results on magnetism of pure C\textsubscript{60}, C\textsubscript{70} and higher fullerenes. The main features of the structure and the magnetic properties of intercalated fullerenes, such as metallofullerenes, TDAE-C\textsubscript{60} and polymeric A\textsubscript{1}C\textsubscript{60}, are presented. Attention is also paid to the mixed state properties of fullerene superconductors, especially to the evaluation of the critical fields and the characteristic lengths of these materials. Some new experimental results on this subject are also presented.

1. Introduction
The history of fullerenes started in 1984, when Rohlfing et al. [1] and shortly later Kroto et al. [2] discovered a new stable form of solid carbon, namely carbon clusters C\textsubscript{n}, in addition to the previously known forms, i.e. solid networks, graphite and diamond. The relationship between the crystal structure of graphite, diamond and the C\textsubscript{60} fullerene as well as their relative binding energies per carbon atom are shown in Fig. 1. In honour of the architect R. Buckminster Fuller this new molecule was called the buckminsterfullerene or fullerene. The latter is now used mainly for the C\textsubscript{60} molecule, while other C\textsubscript{n} clusters are usually called fullerites. Because of the spherical shape of C\textsubscript{60}, this molecule is sometimes called ‘soccerball’ or ‘buckyball’.

C\textsubscript{60} consists of 12 pentagons and 20 hexagons, while the nearest neighbour fullerite molecule C\textsubscript{70} consists of 12 pentagons and 25 hexagons and has a slightly ellipsoidal shape (Fig. 2).

During the first six years after their discovery, fullerenes were considered as exotic materials and investigated mainly theoretically. In 1990 Krätschmer et al. [3] discovered a very simple method to extract fullerenes from carbon soot. Since then intensive experimental and theoretical investigations of these materials have started. During this short time they have become one of the most fascinating and rapidly developing areas of modern science.

The materials are indeed interesting for many scientific areas such as chemistry, physics, materials science, biology, and partly ‘chemical engineering’. Many

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Fig. 1. Relationship between the crystal structures of the three forms of carbon and their relative binding energies per carbon atom. Under normal conditions energy barriers prevent the spontaneous conversion of $C_{60}$ to diamond or graphite. [From Ref. 23]

Fig. 2. Molecular structures of three fullerenes isolated in pure form. [After Ref. 16]
Fig. 3. (a) Electron micrographs showing commonly found multi-shell carbon nanotubes. (b) Formation of quasi-spherical onionlike particles under electron irradiation: (a) Polyhedral particle as obtained from the electric arc; (b) after 20 s of irradiation the particle collapses and the inner central empty space disappears; (c) after 120 s the reordering begins at the surface and progresses to the centre—at this point we see several closed surface layers and an incompletely formed core; and (d) after 180 s, further irradiation yields a quasi-spherical onion-like particle with a very small central shell. [After Ref. 247]
different shapes of fullerenes are observed experimentally, such as carbon sheets, which consist of hexagons only, tubes with open and closed (if pentagons are present in the structure) ends, tubes having different diameters (Fig. 3a), buckyonions (Fig. 3b), which consist of different fullerites placed inside each other, bamboos, spirals, etc. These shapes are illustrated in Fig. 4.

More than one thousand publications on fullerene physics, chemistry, materials science, biology, etc. have appeared in scientific journals each year since 1990. Special journal issues [4–8] and a special monthly journal, *Fullerene Science and
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Technology’, are devoted to this subject. One can find large numbers of books and reviews on the chemical, physical and structural properties of these substances [9–38]. The latter papers overview different subjects of fullerene research. Only one review [38] exists to date, which discusses the magnetic properties of fullerene superconductors. However, because of the large number of experimental results obtained on magnetic properties of different intercalated fullerene compounds, it is worth while, even briefly, to summarise our knowledge of this field.

In this paper an attempt is made to highlight some experimental results on solid state and magnetic properties of fullerenes. We do not discuss all the features in detail, but rather refer the reader after a short discussion to original publications given in the reference section.

This paper is organised as follows. In the next section, we discuss the solid state structure and the magnetism of the undoped $C_{60}$ and $C_{70}$ fullerenes, and higher fullerites. In Section 3, we present the main features of the metallofullerenes, the TDAE-$C_{60}$ derivatives and the polymeric $AC_{60}$ compounds. The section on superconductivity of fullerenes discusses the background of superconductivity in the graphite intercalated compounds and shows results on their normal state properties and their magnetic features in the superconducting state. In Section 5, we present the main experimental results on the critical fields and discuss different methods to obtain the lower critical field of fullerene superconductors. In the last two sections we will discuss flux pinning problems in this type of superconducting materials and address some unsolved questions on the magnetic properties of fullerenes.

2. Solid State Structure of Undoped Fullerenes

Fullerenes are black insulating materials with face centred cubic structure (fcc) at room temperature. The cage diameter of $C_{60}$ is 0.71 nm and the lattice constant is 1.42 nm. The main physical properties of carbon $C_{60}$ are summarised in Table 1.

The magnetism of fullerenes has been of interest since their discovery. The large diamagnetism of graphite suggests that the fullerenes might also display strong $\pi$-electron ring currents and an enhanced magnetic susceptibility. Furthermore, if $C_{60}$ is viewed as a sphere with 60 free electrons, which can respond to the application of a magnetic field, the ring current diamagnetism is expected to be 41 times that of benzene [39]. However, despite the trigonal bonding configuration, which is similar to that of graphite, the susceptibility $\chi$ of $C_{60}$ (Fig. 5) is more than one order of magnitude smaller than that of graphite.

Calculations based on the London theory predicted a vanishingly small $\pi$-electron ring current magnetic susceptibility due to the cancellation of the diamagnetism by a very strong Van Vleck paramagnetic term [39, 40]. Experimental results on the magnetic susceptibility of bulk fullerenes confirmed the basic findings of the London calculations [41, 42]. A further treatment shows that the smallness of $\chi$ comes from the presence of both five-membered rings (5-MRs) and six-membered rings (6-MRs), which have paramagnetic and diamagnetic ring currents, respectively [43, 44]. The near cancellation of the ring current contributions to $\chi$ is due to the unique arrangement of the 5-MRs and the 6-MRs in $C_{60}$. This is illustrated by considering $C_{70}$, the susceptibility of which is larger by a factor of 2 than
that of C$_{60}$ despite its structural similarity to C$_{60}$ [41, 42]. Because undoped C$_{60}$ is a semiconductor, there is no contribution to $\chi$ from conduction electrons. Thus, $\chi$ is a good probe of the intramolecular electronic structure.

Table 1a. Properties of solid C$_{60}$ [after Ref. 23]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>1.67 g cm$^{-3}$</td>
<td>[51]</td>
</tr>
<tr>
<td>fcc lattice constant</td>
<td>1.4198 nm</td>
<td>[51]</td>
</tr>
<tr>
<td>Nearest neighbour distance</td>
<td>1.004 nm</td>
<td>[51]</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>14–18 GPa</td>
<td>[230, 231]</td>
</tr>
<tr>
<td>Young’s modulus (solvated crystal)</td>
<td>16 GPa</td>
<td>[57]</td>
</tr>
<tr>
<td>Vickers hardness</td>
<td>14–5–17.5 kg cm$^{-2}$</td>
<td>[232]</td>
</tr>
<tr>
<td>Volume thermal expansion coefficient</td>
<td>6.2×10$^{-4}$ K$^{-1}$</td>
<td>[233]</td>
</tr>
<tr>
<td>Heat of sublimation</td>
<td>140–160 KJ mole$^{-1}$</td>
<td>[228, 229]</td>
</tr>
<tr>
<td>Vapour pressure (500°C)</td>
<td>6.59×10$^{-4}$ mbar</td>
<td>[228]</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.4 W mK$^{-1}$</td>
<td>[55]</td>
</tr>
<tr>
<td>Debye temperature</td>
<td>74 K</td>
<td>[234]</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.90</td>
<td>[235]</td>
</tr>
<tr>
<td>Dielectric constant, static</td>
<td>4.4</td>
<td>[236, 237]</td>
</tr>
<tr>
<td>Optical absorption edge</td>
<td>1.5–1.7 eV</td>
<td>[237–40]</td>
</tr>
<tr>
<td>Transport energy gap</td>
<td>1.9 eV</td>
<td>[241]</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td>$\sim$10$^{14}$ Ω cm</td>
<td>[241]</td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
<td>$-0.35\times10^{-9}$ A m$^2$</td>
<td>[41, 42]</td>
</tr>
</tbody>
</table>

Table 1b. Properties of the C$_{60}$ molecule [after Ref. 23]

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cage diameter</td>
<td>0.71 nm</td>
<td>[242]</td>
</tr>
<tr>
<td>Intrapentagon C-C distance</td>
<td>0.145 nm</td>
<td>[242]</td>
</tr>
<tr>
<td>Interpentagon C-C distance</td>
<td>0.140 nm</td>
<td>[242]</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>2.65 eV</td>
<td>[243]</td>
</tr>
<tr>
<td>Ionisation potential</td>
<td>7.61 eV</td>
<td>[244]</td>
</tr>
<tr>
<td>Binding energy/atom</td>
<td>7.0 eV</td>
<td>[245]</td>
</tr>
<tr>
<td>(calculated)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polarisability (calculated)</td>
<td>8.0 nm</td>
<td>[246]</td>
</tr>
</tbody>
</table>

Calculations on high-symmetry giant fullerenes C$_n$ in the size regime $100 < n < 1000$ [45] demonstrate that $\chi$ increases monotonically towards the graphite value (Fig. 6). The nanotubes, i.e. higher fullerenes, are also a very interesting subject for magnetic investigations. It was shown [46] from band structure calculations, that the electronic structure of nanotubes is highly sensitive to the degree of helicity of the carbon atom network [47]. Three different categories of helicity are identified, each with its particular band structure. In general, however, the band gap scales with helicity, except for high-symmetry configurations. Because of the interband processes, which lead to the large band
gaps in graphite, it is apparent from the present data that the majority of tubes have a narrow gap band structure similar to that of graphite. DC magnetic experiments [48] showed also an anisotropy of the magnetic susceptibility in carbon nanotubes.

![Graph showing magnetic susceptibility of various forms of carbon](image1)

**Fig. 5.** Orientationally averaged magnetic susceptibility of various forms of carbon. [From Ref. 46]

![Graph showing π-electron ring current magnetic susceptibilities](image2)

**Fig. 6.** The π-electron ring current magnetic susceptibilities $\chi_{RC}$ as a function of fullerene size $n(C_n)$, calculated with resonance integrals adjusted for bond strength. [From Ref. 45]
It is well known, that among the fullerenes, the \( \text{C}_{60} \) molecules have the highest cohesive energy per atom and are the most abundant. This is one of the reasons why the \( \text{C}_{60} \) fullerene receives primary attention. Having near-spherical shape, these molecules form at low pressures crystal lattices of cubic symmetry. The low temperature phase of the \( \text{C}_{60} \) fullerene is orientationally ordered and consists of four simple cubic sublattices, which differ from each other by the orientations of the molecules [49, 50]. It is often referred to as the simple cubic (sc) lattice, although it closely resembles the face centred cubic lattice apart from the orientations of its molecules.

Because of their spherical shape, \( \text{C}_{60} \) molecules can freely rotate in the lattice at high temperatures and the thermal behaviour of solid \( \text{C}_{60} \) shows several phase transitions due to the orientational re-ordering of \( \text{C}_{60} \) molecules. At room temperature, solid \( \text{C}_{60} \) has an fcc crystal structure. The molecules are in complete orientational disorder and form a ‘plastic crystal’ [49, 51, 52]. With decreasing temperature the system undergoes a first order transition to the sc crystal structure at \( T \sim 260 \) K [52, 53]. The transition is due to orientational re-ordering, although significant disorder persists to low temperatures [54, 55]. The population of the dominant orientation increases with decreasing temperature down to \( T \sim 90 \) K, where 83·3% of the molecules are in the dominant orientation. This occupancy does not change at lower temperatures [54].

At this temperature a glass transition was predicted theoretically [56] and anomalies were observed experimentally by neutron diffraction [54], sound velocity [57], dielectric constant [58], high-resolution dilatometry [59], specific heat [60] and other techniques. Arguments were presented [59–61] that this transition would lead to a frozen glass state. At this temperature, an interesting magnetic behaviour was observed in iodine doped \( \text{C}_{60} \) [62–65]. Buntar et al. [62] performed detailed measurements of \( \text{C}_{60} \), \( \text{C}_{70} \) and \( \text{I-C}_{60} \) at low temperatures and observed an irreversibility of the magnetisation at \( T < 100 \) K and a strong extremum at \( T \sim 60 \) K (Fig. 7). These authors showed that the magnetic phenomena could be due to a transition into a frozen magnetic state.

Fig. 7. Temperature dependence of the magnetisation of \( \text{I}_2\text{C}_{60} \) at \( \mu_0H_{\text{ext}} = 50 \) mT. [From Ref. 62]
In the low temperature modification of solid C\textsubscript{60}, the non-central part of the intermolecular potential leads to orientational ordering of the molecules \cite{66, 67}, whereas in the high temperature phase it disappears after averaging over all orientations of the rapidly rotating molecules. Ref. \cite{68} gives a complete set of the thermal and elastic properties in the fcc modification in particular for the high temperature phase.

Unlike the spheroidal C\textsubscript{60} molecule, the C\textsubscript{70} molecule has an ellipsoidal shape. This results in an additional degree of freedom for ‘packing’ the solid and implies that the orientational ordering of the oblong C\textsubscript{70} solid is much more complex. Vaughan \textit{et al.} \cite{69} reported hexagonal close packed (hcp) and fcc structures for C\textsubscript{70} crystals. Their X-ray and electron microscopy measurements revealed the presence of more defects than in C\textsubscript{60}. Fleming \textit{et al.} \cite{70} also reported fcc and monoclinic phases. Verheijen \textit{et al.} \cite{71} found four types of structure: fcc at high temperature, rhombohedral (rh), ideal hcp, and deformed hcp around room temperature. Several groups also reported similar structures \cite{72-75}. It is well accepted now that the thermodynamically stable form of sublimed C\textsubscript{70} is the cubic close packed one (see for instance Ref. 76).

The rotation dynamics in both the ordered and the disordered phases of C\textsubscript{70} were studied by a number of experimental techniques such as \textsuperscript{13}C NMR \cite{77-79}, muon spin relaxation \cite{80, 81} and inelastic neutron scattering \cite{82, 83}. At very high temperatures, the orientational motion is described as quasi-isotropic, much like in C\textsubscript{60}. The first evidence for anisotropy in the motion appears at T \approx 370 K, well within the temperature regime of the fcc phase.

3. Intercalated Fullerenes

A large number of chemical elements are considered as intercalants in solid M\textsubscript{2}C\textsubscript{60} compounds or in free M@C\textsubscript{60} (the symbol @ indicates that the metal atom M is encaged in the fullerene molecule) endothedral complexes or metallofullerenes (see for instance Fig. 2 in Ref. 84). The discovery of C\textsubscript{60} was soon followed by that of C\textsubscript{60} with metals encaged, the metal atom being either La or an alkali earth atom \cite{85}. The name ‘metallo-fullerenes’ has now become common to denote fullerenes with a metal atom inside. The first type of metallofullerene extracted from fullerene soot was lanthanum-fullerene La@C\textsubscript{82} \cite{86-89} followed a short time later by scandium fullerene Sc@C\textsubscript{82} \cite{90, 91} and yttrium fullerene Y@C\textsubscript{82} \cite{90, 92}.

Charge transfer to the fullerene units leads to salt or donor–acceptor adduct formation. Intercalation of solid C\textsubscript{60} with electron donors, like the alkali metals, results in salts with stoichiometries A\textsubscript{x}C\textsubscript{60} with x up to 12 for Li\textsubscript{12}C\textsubscript{60}. In addition, fullerenes can be intercalated with different organic molecules such as TDAE, tetrakis(dimethyl-amino)ethylene \cite{93}, TTF (tetraphiafulvalene) \cite{94}, and others.

(3a) Magnetic Fullerene Derivative TDAE-C\textsubscript{60}

Among the compounds based on C\textsubscript{60}, the organic molecule TDAE-C\textsubscript{60} raised quite a lot of interest due to its ferromagnetic-like phase transition at T = 16 K (Fig. 8) \cite{93}. Furthermore, the TDAE-C\textsubscript{60} material has the highest T\textsubscript{c} of any molecular organic ferromagnet.
Fig. 8. DC magnetisation as a function of temperature for a pellet of TDAE-C$_{60}$ in an applied field of 0·1 mT. The inset gives the isothermal magnetisation at 5 K. [From Ref. 249]

TDAE is one of the strongest organic donors. In the 1:1 stoichiometry each TDAE molecule donates one electron to the band formed by the lowest unoccupied $t_{1u}$ molecular orbit (LUMO) of the C$_{60}$ units. The crystal is monoclinic [95], with a shorter C$_{60}$-C$_{60}$ distance along the $c$ axis, and displays ‘activated’ DC transport properties characteristic of large gap semiconductors [96, 97], or rather a Mott–Hubbard insulator [98].

Several experiments have confirmed by now that TDAE-C$_{60}$ undergoes a soft ferromagnetic spin-glass or superparamagnetic ordering transition below $T_c$, where the magnetisation versus magnetic field curves become S shaped and strongly nonlinear [93, 99]. Evidence for a magnetic hysteresis curve in TDAE-C$_{60}$ was also reported [100].

The magnetic behaviour is still controversial. Experiments on earlier samples indicated signatures of weak and/or disordered magnetism. Spin glass features were seen in AC susceptibility [101], capacity [102], electron spin resonance (ESR) [103] and muon rotation ($\mu$SR) [104] measurements. More recently, long range order was inferred from the rather narrow local magnetic field distribution probed by implanted muons [105, 106], and from single crystal ESR [107]. The strongly anisotropic ESR line intensity was interpreted in terms of an antiferromagnetic exchange along the $c$ axis, leading to weak ferromagnetism of the Dzyaloshinsky–Moria type [108, 109].

Growing experimental evidence points towards a fundamental role played by the orientational (merohedral) order of the Jahn–Teller distorted fullerene molecules for the magnetic properties of this compound. It suggests that the degree of merohedral order, established when the C$_{60}$ orientational degrees of freedom become frozen (at the plastic phase transitions), controls the nature of exchange paths among neighbouring molecules. In particular recent AC susceptibility and ESR measurements [110] show large variations of the magnetic response upon different cooling procedures, from the room temperature plastic phase across the
first freezing temperature of the rotational dynamics of $C_{60}$. A ten-fold increase of $\chi''$ is observed below $T_c$ for slowly cooled versus quenched samples.

TDAE-higher-fullerite complexes such as TDAE-$C_{70}$, -$C_{84}$, -$C_{90}$, and -$C_{96}$ do not show a ferromagnetic transition, but only paramagnetism at least above 4.5 K [99, 111, 112]. The fact that no magnetic transition was observed in TDAE-$C_{70}$ provides additional evidence that the radical spins reside mainly on the fullerenes. Moreover, the strong narrowing of the ESR line with decreasing temperature together with the observation of relatively high ambient temperature conductivity on a pressed pallet ($10^{-2}$ Ω cm$^{-1}$) have led to the speculation that TDAE-$C_{60}$ might be metallic and therefore an itinerant ferromagnet [93]. Very recent measurements [96, 113] of the microwave conductivity and optical experiments indicate a clear nonmetallic temperature dependence of the conductivity with a value of the order of $10^{-4}$ Ω cm$^{-1}$ at 300 K. These authors placed TDAE-$C_{60}$ into the class of semiconducting systems without long-range structural order, where electron localisation eventually leads to a hopping process for electrical transport [96, 113].

![Fig. 9. Structures of $C_{60}$ and $A_xC_{60}$, where $C_{60}$ is represented by a large sphere and $A$ by a smaller sphere: (a) fcc $C_{60}$ drawn in an equivalent bct representation; (b) structure of $Na_2C_{60}$ with Na ions in the tetrahedral interstitial sites; (c) $A_3C_{60}$ with A ions in both tetrahedral and octahedral interstitial sites; (d) $A_4C_{60}$ structure ($A = K, Rb$ and Cs); (e) fcc $A_6C_{60}$ structure ($A = Na, Ca$) with the darker Na 50% occupied; and (f) bcc $A_6C_{60}$ structure ($A = K, Rb$ and Cs). [From Ref. 250]]
(3b) Alkali Metal Doped Fullerenes

In the beginning, it was believed that only $x = 2, 3, 4$ and 6 stoichiometries are stable for alkali metal doped fullerenes $A_xC_{60}$. The structures of these compounds are shown schematically in Fig. 9. Shortly after the $A_1C_{60}$ systems were discovered [114], they attracted much interest because of their unusual structural, magnetic and electrical properties. These materials were identified from a Raman analysis of the potassium compound. From X-ray structural investigations the compound was found to have an fcc lattice with a rocksalt structure, where the potassium ions are located on the octahedral interstitial lattice sites [115, 116].

The alkali fullerites $AC_{60}$ (where $A = K, Rb$ and $Cs$) have a number of stable and metastable modifications. At $T = 370$ K they undergo a first order structural transition from a high temperature fcc to a low temperature orthorhombic phase [117–120]. The structure of this new low temperature phase is quite interesting, since a detailed X-ray investigation [118] resulted in unusually short $C_{60}–C_{60}$ distances along the [110] direction of the original fcc lattice, i.e. only 0.912 nm. This distance implies that the separation between nearest neighbour molecules along the $c$ axis is as small as $\sim0.2$ nm, which has led to the suggestion that the fullerene molecules in this phase polymerise to form an ordered crystalline array of quasi-one-dimensional chains, resembling a lattice of aligned ‘necklaces’ of fullerene molecules. This polymerisation process is stereochemically similar to the photopolymerisation of $C_{60}$ suggested by Rao et al. [121].

For the heavier alkalis (Rb, Cs) this orthorhombic phase undergoes a second electronic phase transition below 50 K. ESR spin susceptibility measurements [117, 122] indicate a magnetic transition at $T \sim 50$ K. The results are shown in Fig. 10. Chauvet et al. argued that this was a transition to a spin density wave state. However, detailed electronic structure studies [123, 124] do not support this interpretation. Moreover, several $\mu$SR studies [125–28] are consistent with a disordered magnetic phase and not with long range spin density wave order. This magnetic transition is accompanied by a metal–insulator transition [129]. CsC$_{60}$ was found to behave similarly to RbC$_{60}$ in this respect, but KC$_{60}$ was recently claimed to be metallic down to very low temperatures [129].

Metastable phases of monomer $C_{60}^–$ ions or $(C_{60}^–)_2$ dimers were formed by quenching the samples from high temperature to below 300 K [130–33]. Various phase transitions between these phases were reported [134].

Deep quenching of CsC$_{60}$ and RbC$_{60}$ leads to a metallic monomer phase [135], the structure of which was found to be primitive cubic (Pa3) by high resolution powder neutron diffraction [136]. This is the only cubic phase of a binary $C_{60}$ salt with a stoichiometry different from $A_3C_{60}$ that is metallic.

4. Superconductivity of Fullerenes

(4a) Background of Fullerene Superconductivity

Superconductivity in graphite intercalation compounds has been known since 1965 when Hannay et al. [137] reported transition temperatures in alkali metal graphite intercalation compounds up to 0.55 K for CsCs. In the past few years, high pressure synthesis allowed preparation of samples with higher concentrations of alkali metals and resulted in binary graphite intercalated compounds with superconducting transition temperatures as high as 3 K in C$_3$K and 5 K in C$_2$Na.
Another interesting class of superconducting graphite intercalated compounds, e.g. C₄KTl₁·₅ (Tₑ = 2·56–2·7 K), also becomes superconducting as 'second stage compounds' such as C₃KTl₁·₅ (Tₑ = 1·3–2·45 K).

Conductivity [138] and superconductivity [139, 140] of the alkali-metal doped fullerenes were discovered less than one year after the production method for bulk quantities of C₆₀ and C₇₀ had been published [3]. The phenomenon of superconductivity is one of the most fascinating properties of 'the roundest of all round molecules' [11], which attracted enormous scientific interest in this new form of carbon. In many aspects the situation was similar to that shortly after the discovery of superconductivity at high temperatures in the copper oxides [141, 142]. Fullerene superconductors were the second group of materials besides the cuprates, which overcame the previous boundary for the critical temperature, Tₑ = 23·2 K (Nb₃Ge), in conventional superconductors. More than twenty superconducting compounds of doped fullerenes have been synthesised by now. The highest critical temperature (Tₑ = 33 K) occurs in the fullerene RbCs₂C₆₀ [143]. (Palstra et al. [144] reported superconductivity in Cs₃C₆₀ with Tₑ = 40 K at high pressure; however, this result has not yet been reproduced.) These new superconducting compounds can be prepared easily by heating alkali metal–C₆₀ mixtures at T ~ 300°C or by keeping C₆₀ in an alkali metal vapour atmosphere. However, to get from the synthesis of individual samples to practical applications of these superconductors, numerous investigations of the physical properties, stability, reproducibility, and the elaboration of technologies for the production of large quantities for technical use are required. One of the biggest
problems is their instability against air. It is enough to expose the material to air for a fraction of a second to completely destroy superconductivity.

Numerous experimental investigations of these superconductors, both in granular and in crystalline form, show unique properties and distinguish them from other superconducting materials. It was shown (see for instance Ref. 145) that superconductivity in alkali metal doped fullerenes occurs in the face centred cubic (fcc) crystal phase with the composition \( A_xB_{3-x}C_{60} \) [146]. Other crystalline phases, such as body centred cubic (bcc) and body centred tetragonal (bct), do not show superconductivity. In the other family of fullere superconductors, i.e. alkali-earth-doped \( C_{60} \), superconductivity occurs in simple cubic \( Ca_5C_{60} \) [147] and in bcc \( Sr_6C_{60} \) [145] and \( Ba_8C_{60} \) [148]. (An additional phase, possibly \( Ba_4C_{60} \), was found from X-ray diffractometry and there is some evidence [149] that this phase could be responsible for the occurrence of superconductivity in Ba compounds.) Intercalation of fullerenes with rare-earth (RE) metals Yb, Sm and Eu has led to superconductivity in \( RE_{2.75}C_{60} \) compounds with \( T_c \approx 6 \) K [150]. Furthermore, a superconducting phase in the lanthanum fullerite \( La_xC_{60} \) was found from microwave absorption measurements below 12.5 K [150].

New silicon clathrate compounds containing barium with an alkali metal, \( (Ba, A)_xSi_{46} \) (\( A = Na, K \)), have recently been synthesised and reported to be superconducting [151–54]. The barium containing clathrate compounds as well as the \( C_{60} \) based ones are type-II superconductors with a \( T_c \) of about 4 K. Diamagnetism due to superconductivity was observed [151] in good agreement with resistivity measurements. Chemical analysis showed that the compositions of the clathrates were close to the ideal composition of \( Ba_6A_2Si_{46} \). The silicon clathrate compound consists of a Si-sp\(^3\) open network having two types of cages, \( Si_{20} \) pentagonal dodecahedra and \( Si_{24} \) tetrakaidecahedra, the two types of polyhedra being linked by shared faces. The X-ray Rietveld analysis shows that the alkali metal atoms mainly occupy the former and the barium atoms the latter cages. This is the first superconductor found for a Si-sp\(^3\) covalent network.

One of the most important results is the experimentally established empirical linear correlation of the transition temperature \( T_c \) both with the lattice constant of the cubic structure \( a \) [143, 146, 155, 156] and with the density of states at the Fermi level [157–59]. Transition temperatures of different \( A_xC_{60} \) superconductors versus the fcc lattice parameter \( a \) are shown in Fig. 11. This relationship also holds for the corresponding alloys as well as for these materials under lattice compression [160, 161] (Fig. 12). The slope of this linear \( T_c(a) \) relation depends on the structural type [162–64]. Very recently [165], a second much steeper \( T_c(a) \) dependence was found for the space group P\( a \) [166], which could lead to much higher \( T_c \) values if only a slight increase in a could be achieved (see Fig. 13). Fig. 13 also shows a difference between ambient (solid line) and high pressure (dotted line) data, in contrast to the case of the fcc superconductors where both sets of data coincide.

(4b) Normal State Properties

Doping \( C_{60} \) with alkali metals leads to a change of its electrical resistivity from very high values (\( 10^8-10^{10} \) Ω cm for \( C_{60} \)) to a metallic-like behaviour in \( A_xC_{60} \), because the doping results in a charge transfer to the \( C_{60} \) molecules and strongly increases the \( \pi-\pi \) overlap between them, enhancing the electrical
conductivity. The electrical resistivity $\rho$ approaches a minimum at $x = 3$, where it reaches typical values of high resistivity metals [167, 168]. The low electrical conductivity can be explained by the relatively weak overlap of the electron wavefunctions between the adjacent $C_{60}$ ions and by the merohedral disorder in the alignment of adjacent $C_{60}$ ions.

![Graph showing variation of superconducting transition temperature $T_c$ with fcc lattice parameter $a$ for various compositions of $A_3C_{60}$.](image)

Xiang et al. [169] measured the resistivity of single crystal $K_3C_{60}$ and obtained a metallic behaviour $\rho(T)$ between 20 and 300 K, with a residual resistivity of 2.5 m$\Omega$ cm. Hebard et al. [170] reported measurements of the resistivity $\rho(T)$ for both $K_3C_{60}$ and $Rb_3C_{60}$ thin films. The results revealed a metallic behaviour up to 520 K without any evidence for saturation and a linear temperature dependence of the resistivity above 300 K. For $Rb_3C_{60}$ they found that the residual resistivity was about 1.1 m$\Omega$ cm, which is less than that reported in Ref. [169]. Based on a spherical Fermi surface and on the traditional Bloch–Boltzmann approximation, the authors obtained the transport scattering length $l_{tr} = 0.063$ nm calculated from $\rho(520 K) = 5.5$ m$\Omega$ cm, which is significantly shorter than the nearest neighbour distance between the $C_{60}$ molecules (1 nm) and the average separation of 0.6 nm between the conduction electrons, and even shorter than the distance between neighbouring C atoms in each $C_{60}$ molecule (0.14 nm). Even for the residual resistivity (1.1 m$\Omega$ cm) we still get $l_{tr} = 0.3$ nm, which is too short. All this seems to indicate that the electron is for the most part confined within the surface of a given molecule before hopping to the next one. In addition, the transport electron–phonon coupling constant $\lambda_{tr}$ was estimated in Ref. [170] and
Fig. 12. The inset shows the temperature dependence of the magnetic susceptibility of polycrystalline pressed pellets of Rb$_3$C$_{60}$ at various pressures. The lower transition $T^*$ is indicative of an intergranular coherence transition. The bulk superconducting transition $T_c$ is determined as the point of highest curvature. The pressure dependence of $T_c$ is shown for both K$_3$C$_{60}$ and Rb$_3$C$_{60}$. The solid and open symbols correspond to data taken under increasing and decreasing pressure, respectively. The K$_3$C$_{60}$ data have been shifted by 1.06 GPa, and the two data sets have the same pressure dependence $T_c(P) = T_c(0)\exp \left(-\gamma P\right)$, where $\gamma = 0.44 \pm 0.03$ GPa$^{-1}$. [From Ref. 249]

Fig. 13. Plot of $T_c$ versus $a$ for Fm3m [143, 156] and Pa3-ordered superconductors [166]. Solid and dashed lines are fits to McMillan’s formula using linear and power law dependencies, respectively, of $N(E_F)$ on the intermolecular distance; only the parameters describing $N(E_F)$ versus $a$ differ in the fits for the two families of materials. The slope of the Pa3 curve is much larger than that for Fm3m, indicating that a small increase of $a$ without destroying Pa3 ordering should cause $T_c$ to increase very rapidly. The dotted line represents the results of Ref. [251]. [After Ref. 166]
found to be $\lambda_{tr} = 4.4$ for Rb$_3$C$_{60}$, i.e. clearly strong coupling. Both of these results, a short $\lambda_{tr}$ and strong electron–phonon coupling, indicate predominant intramolecular electron–phonon interaction.

Vareka et al. [171] found that under conditions of constant sample volume the normal state resistivity of Rb$_3$C$_{60}$ has a linear temperature dependence, $\rho \sim T$, in sharp contrast to $\rho \sim T^2$ observed under conditions of constant sample pressure. This result is important because positive $\delta \rho(T)/\delta T$ is consistent with metallic behaviour and the linear term in the temperature dependence of $\rho(T)$ is consistent with an electron–phonon scattering mechanism.

Measurements of the magnetic susceptibility $\chi$ in the normal state by Ramirez et al. [158] and by Wong et al. [172] demonstrated that the susceptibility was positive. The susceptibility $\chi(T)$ was found to be temperature independent, consistent with the metallic Pauli susceptibility.

More results and discussions of the normal state scattering mechanisms can be found in Refs [33, 34, 173–78].

\textbf{(4c) Magnetisation Curves}

The first experiments on K$_3$C$_{60}$ [179] and Rb$_3$C$_{60}$ [180, 161] established that alkali doped fullerenes were ‘strong’ type-II superconductors and that their main superconducting parameters, the Ginzburg–Landau parameter $\kappa$, the penetration depth $\lambda$, the coherence length $\xi$, and the critical fields $H_{c1}$ and $H_{c2}$, were very similar to those of the high-$T_c$ oxides.

Typical temperature and magnetic field dependencies as well as the time relaxation of the magnetisation $M$, measured on K$_3$C$_{60}$ and Rb$_3$C$_{60}$ superconductors [180, 181] with a SQUID magnetometer, are shown in Figs 14, 15 and 16 [182]. We wish to point out, that the ZFC magnetisation shows the flux exclusion from the sample, while the FC magnetisation shows the flux expulsion. A big difference between zero-field-cooled (ZFC) and field-cooled (FC) curves (Fig. 14) and a strong hysteresis in the magnetic field dependence of the magnetisation at fixed temperature (Fig. 15) indicate pinning of the magnetic vortices. The fact that the FC signal of the K$_3$C$_{60}$ crystal (Fig. 14) is very small and lies close to the zero-magnetisation line shows that pinning in the sample is extremely strong and that there is almost no expulsion of the magnetic field.

The magnitudes of the ZFC and FC magnetisation at the lowest temperature can be used for an evaluation of the ‘superconducting fraction’ $X_{sc}$. The fraction can also be evaluated from the slope of the linear dependence of $M$ on $H$ at $H < H_{c1}$. The latter method was used in Refs [183, 184] and appears to be better than the former.

Detailed discussions of these evaluations can be found in Ref. [38], where we pointed out that a quantitative evaluation of $X_{sc}$ is difficult, especially for powdered samples, and should be done very carefully. Almost all of the superconducting volume fractions published for fullerene superconductors were obtained from ZFC measurements and vary between 40 and 90% in powder samples [146, 148, 185–88]. We believe that these values should be treated as a lower limit because of granularity effects [189, 190].
Fig. 14. Temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) d.c. magnetic susceptibility of K$_3$C$_{60}$ crystals with 65% superconducting fraction (K3) and 100% superconducting fraction (K5 and K6). The difference in the absolute value of $\chi$ for K5 and K6 is due to the influence of the geometrical demagnetisation factor. [From Ref. 203]

Fig. 15. Hysteresis loops for Rb$_3$C$_{60}$ powder at (a) $T = 7$ K and (b) $T = 20$ K. [From Ref. 180]
Fig. 16. Time dependent magnetisation in an external magnetic field $\mu_0 H_{\text{ext}} = 0.1 \, \text{T}$ at 5, 7, 10 and 15 K. [From Ref. 182]

5. Critical Fields and Characteristic Lengths of Fullerene Superconductors

(5a) Upper Critical Field and Coherence Length

A large number of experiments was made to determine the upper critical field for crystalline [169, 175, 181, 191–93] and powdered [159, 161, 179, 180, 183–85, 190, 194–98] fullerenes as well as for thin films [176] using different techniques such as magnetisation [161, 179, 180, 184, 198], ac-susceptibility [190, 195], transport [176, 197], rf-absorption [196], etc. Almost all measurements were done on $\text{K}_3\text{C}_{60}$ and $\text{Rb}_3\text{C}_{60}$ and only a few results are available on each of $\text{RbCsC}_{60}$ [184], $\text{K}_2\text{CsC}_{60}$ and $\text{Rb}_2\text{CsC}_{60}$ [199] and $\text{Ba}_6\text{C}_{60}$ [200]. Other superconducting fullerenes have not yet been characterised.

Typical results on the temperature dependence of the upper critical field are shown in Fig. 17. Measurements of $H_{c2}$ are limited by the experimentally achievable magnetic fields, which are usually not larger than 5–8 T. The extrapolation of $H_{c2}(T)$ to zero is subject to a large uncertainty and depends on the fitting scheme. The standard theory by Werthamer–Helfand–Hohenberg (WHH) [201] is usually employed. This theory predicts an $H_{c2}(T)$ dependence, which follows roughly a power law $h = 0.6 (1 - t^\alpha)$, where $t = T/T_c$, $h = H/H_{c2}$ and $\alpha \approx 1.75$. Here $H_{c2}(0)$ can be evaluated from the slope, $H'_{c2}$ near $T_c$. In order to verify the applicability of this relation to $\text{C}_{60}$-based materials, several experiments were performed up to very high magnetic fields [194–96]. Good agreement of the experimental data with the WHH prediction was obtained [194–96] demonstrating that this theory is successful in describing fullerene superconductors (Fig. 18).
Fig. 17. Temperature dependence of the upper critical field $H_{c2}$. The inset indicates the method for determining $T_c$ from magnetisation data at different magnetic fields. [From Ref. 161]

Fig. 18. Upper critical field versus temperature for (a) K$_3$C$_{60}$ powder and (b) Rb$_3$C$_{60}$ powder. The low field data are taken in d.c. fields and the data points at 4.2 K are taken in pulsed fields. The lower solid curves are fits to the data (●) including Pauli paramagnetic limiting and the upper curves assume no paramagnetic limiting. Both experimental dependencies follow roughly the WHH prediction [201]. [After Ref. 196]

From $H_{c2}(0)$, the coherence length $\xi$ can be calculated using the Ginzburg–Landau relation [202]

$$\mu_0 H_{c2} = \frac{\Phi_0}{2\pi \xi^2},$$

with $\Phi_0 = h/2e = 2 \times 10^{-15}$ Wb, where $\Phi_0$ is the flux quantum, $h$ is Planck’s constant and $e$ is the electron charge. The coherence length of fullerene superconductors is very small (a few nanometres) and comparable to the short $\xi$ of high-$T_c$ superconductors. According to Ref. [198] the temperature dependence of the coherence length and the penetration depth in Rb$_3$C$_{60}$ can be well described...
by Ginzburg–Landau theory in the temperature range \(0.85 < T/T_c < 1\).

A strong scatter of the experimental data is found for \(H_{c2}(0)\) and \(H'_{c2}\) (Table 2). For example, for \(\text{K}_3\text{C}_{60}\) \(H'_{c2}\) varies from \(-2\) to \(-5.5\ \text{TK}^{-1}\) and for \(\text{Rb}_3\text{C}_{60}\) from \(-2\) to \(-3.9\ \text{TK}^{-1}\). Very recently Buntar et al. [203] performed detailed magnetic measurements of the upper critical field on a bulk \(\text{K}_3\text{C}_{60}\) crystalline sample of a good quality. The temperature dependence of \(H_{c2}\) obtained in this work is shown in Fig. 19. Here \(H_{c2}(T)\) is linear at these temperatures with a slope \(H'_{c2} = -2.1\ \text{TK}^{-1}\), which leads to \(\mu_0 H_{c2}(0) = 28\ \text{T}\) and \(\xi(0) = 3.4\ \text{nm}\).

**Fig. 19.** Temperature dependence of the upper critical field for a sample with 25% superconducting fraction (\(\text{K}1\)—solid squares) and with 100% superconducting fraction (\(\text{K}6\)—open diamonds) and of the irreversibility line (solid triangles) for \(\text{K}1\). [From Ref. 203]

(5b) **Lower Critical Field and Penetration Depth**

The first results on \(H_{c1}\) for \(\text{K}_3\text{C}_{60}\) [179], \(\text{Rb}_3\text{C}_{60}\) [180, 161], \(\text{RbCs}_2\text{C}_{60}\) [184] and \(\text{Ba}_6\text{C}_{60}\) [200] were obtained by a dc-magnetisation technique. The \(H_{c1}(0)\) evaluated from these measurements lies in the range \(\mu_0 H_{c1} = 10–16\ \text{mT}\) (see Table 2). The temperature dependence of \(H_{c1}\) can be described well by \(H_{c1}(T)/H_{c1}(0) = 1–(T/T_c)^2\) [179] and an example of this dependence [204] is shown in Fig. 21 below. From \(H_{c1}(0)\), the penetration depth \(\lambda\) is evaluated using the well known equation

\[
\mu_0 H_{c1} = \frac{\Phi_0}{2\pi\lambda^2} \ln \kappa
\]
and the value of the coherence length known from independent measurements (Section 5a). The magnitude of $\lambda$ obtained in this way is of the order of 200–250 nm (Table 2).

### Table 2a. Experimentally obtained mixed state parameters of fullerene superconductors [after Ref. 215]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$ (K)</th>
<th>$H_{c1}(0)$ (mT)</th>
<th>$H_{c2}(0)$ (T)</th>
<th>$-\Delta H_{c2}$ (T K$^{-1}$)</th>
<th>$\lambda$ (nm)</th>
<th>$\xi$ (nm)</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>19–7 [191]</td>
<td>38 [196]</td>
<td>2.18–2.8</td>
<td>480 [213]</td>
<td>4.4 [190]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>47 [176]</td>
<td>2.8 [196]</td>
<td>600 [218]</td>
<td>4.5 [191]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>49 [179]</td>
<td>3.5 [158]</td>
<td>800 [219]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.73 [179]</td>
<td>590 [181]</td>
<td>5.5 [176]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>76 [196]</td>
<td>3.86 [196]</td>
<td>460 [218]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>78 [161]</td>
<td>3.9 [161]</td>
<td>530 [222]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>800 [219]</td>
<td>850 [181]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$RbCs_2C_{60}$</td>
<td>33 [145]</td>
<td>81 [184]</td>
<td>0.8 [184]</td>
<td>17 [184]</td>
<td>300 [184]</td>
<td>4.4 [184]</td>
<td>68 [184]</td>
</tr>
</tbody>
</table>

### Table 2b. Experimentally obtained superconducting parameters of fullerenes after Ref. [215]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_c$ (A m$^{-2}$)</th>
<th>$2\Delta/k_BT_c$</th>
<th>Activation energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_3C_{60}$</td>
<td>$10^0$ [190]</td>
<td>3.4 [172]</td>
<td>33–55 [182]</td>
</tr>
<tr>
<td></td>
<td>$1.2\times10^0$ [179]</td>
<td>1.76 [212]</td>
<td>10–60 [223]</td>
</tr>
<tr>
<td></td>
<td>$10^0$ [210]</td>
<td>3.52 [179]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$10^1$ [211]</td>
<td>5.2 [224]</td>
<td></td>
</tr>
<tr>
<td>$Rb_3C_{60}$</td>
<td>$10^0$ [190]</td>
<td>3.4 [224]</td>
<td>33 [180]</td>
</tr>
<tr>
<td></td>
<td>$1.5\times10^1$ [161]</td>
<td>4.1 [193]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$2\times10^0$ [198]</td>
<td>5.08 [225]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$4\times10^0$ [180]</td>
<td>7.7 [226]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sim10^0$ [210]</td>
<td>5.4 [227]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\sim10^1$ [211]</td>
<td></td>
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</table>
In these experiments the lower critical field was defined as the field at which a deviation from linearity in $M(H)$ first appeared. Indeed, an ideal superconductor exhibits linear $M(H)$ behaviour up to $H_{c1}$, where a sharp cusp occurs. However, none of the magnetisation data for fullerene materials show good linearity or any cusps (Fig. 20). (The nature of such a behaviour is discussed in Ref. 32.) Usually $M(H)$ has a smooth positive (Fig. 20a) (in some experiments even a negative—see Fig. 20b) curvature. It is extremely difficult to obtain the point of first deviation from such a curve, since the deviations themselves are very small.

In order to make this procedure more quantitative, it is tempting to apply Bean’s critical state model [205] for the entry of vortices into hysteretic superconductors. According to this theory, a plot of $\delta M$ versus $H^2$, where $\delta M = M + H_a$ is the deviation of the observed magnetisation from perfect diamagnetic behaviour, should give the lower critical field. This analysis was done for Rb$_3$C$_{60}$ [204] and RbCs$_2$C$_{60}$ [184]. In Ref. [184] these data agreed well with the data obtained from the first deviation from a linear dependence. However, both methods led to extremely high values of $H_{c1}$ at low temperatures and did not provide us with the ‘intrinsic’ values of the lower critical field. In Ref. [204], the data obtained from Bean’s analysis showed much smaller values of $H_{c1}$ (triangles in Fig. 21) and the authors related their data to the field at which breaking of intergranular Josephson junctions occurs.

The two methods above obviously do not lead to satisfactory results. Therefore, Politis et al. [183] and Buntar et al. [184] used an analysis, which is based on measurements of the reversible magnetisation at high external fields, and calculated $H_{c1}$ from the well known Ginzburg–Landau relations [206]:

$$-M = \frac{H_{c2}(T) - H}{(2 \kappa^2 - 1) \beta_a}; \quad -M = \frac{\alpha \Phi_0}{8 \pi \mu_0 \lambda^2(T)} \ln \frac{\beta H_{c2}(T)}{H}$$

for high and intermediate magnetic fields, respectively. This analysis led to lower critical fields, which were slightly smaller but comparable to the data obtained by the first two methods [183, 184].

The last method, based on direct measurements of the reversible magnetisation at high temperatures, is more accurate for the determination of the lower critical field. However, the resulting values of the Ginzburg–Landau parameter $\kappa$ and, hence, of $H_{c1}$ strongly depend on the value of the superconducting fraction assumed [see Ref. 184, equation (4)]. This leads to an enormous uncertainty in quantitative calculations, especially in the case of powdered samples with a large distribution of grain sizes.

In order to avoid the difficulties associated with the previous three methods, another way to evaluate $H_{c1}$ must be found. In our recent investigations we used a method developed by Böhmer [207], in which $H_{c1}$ is determined through measurements of the trapped magnetisation. This method is far more accurate than the measurements of $\delta M$ because of the cancellation of a large linear contribution [208]. It is based on the fact that trapped magnetic flux, $M_t$, can be built up in a sample only when the field had been increased beyond $H_{c1}$.

The advantage of this method for type-II superconductors with strong pinning was illustrated in Ref. [208], where the $M(H)$ behaviour was shown to appear quite linear in the vicinity of $H_{c1}$, whereas $M_t^{1/2}$ versus $H$ showed a well resolved kink at the field corresponding to $H_{c1}$.
Fig. 20. (a) Magnetic field dependence of the magnetisation of polycrystalline Rb$_3$C$_{60}$ at various temperatures. The inset shows the temperature dependence of $H_{c1}$ [from Ref. 32].

(b) Magnetic field dependence of the magnetisation of polycrystalline K$_3$C$_{60}$ at 5 K [from Ref. 179].
We performed such measurements on RbCs$_2$C$_{60}$ powder and on crystalline Rb$_3$C$_{60}$ and K$_3$C$_{60}$ samples [181]. The magnetic field dependence of $M_t$ at $T = 5$ K for a K$_3$C$_{60}$ single crystal with a shielding fraction of 100% is shown in Fig. 22. Preliminary ac measurements indicate that there is no granularity for current flow in the sample, i.e. there should be no influence of weak links or intergranular boundaries.

As expected, at small fields $H < H_t$, there is no trapped moment, $m$ has some background value and is field independent. When the magnetic field exceeds some characteristic field $H_t$, a trapped moment appears and increases with increasing external field. The $m_t(H)$ dependence follows $m_t \sim H^{1/2}$ as predicted in Ref. [208]. The very unexpected result is that the values of $H_t$ are very small (not higher than 1 mT at zero temperature) in comparison with those values of $H_{c1}$ obtained previously from $\delta M$ measurements. Such small values of $H_t$ are observed for powders and crystals of different quality. Therefore, it is very unlikely that the trapped moment appears at small fields because of granularity or imperfections of the samples. We can certainly state that the lower critical fields of these fullerenes are not higher than the values of $H_t$ observed in these experiments, because the magnetic field has clearly penetrated the sample (Fig. 22). The temperature dependence of the lower critical field for K$_3$C$_{60}$ and Rb$_3$C$_{60}$ crystalline and RbCs$_2$C$_{60}$ powdered samples obtained by measuring the trapped moment is shown in Fig. 18. We obtain the corresponding values of $\lambda$ as 890, 850 and 720 nm. The corresponding Ginzburg–Landau parameters for these compounds obtained from our experimental data are $\kappa = 342$, 315 and 163 respectively.

Small values of the field at which the trapped magnetisation appeared, similar to our results, were also observed by Kraus et al. [209], who measured the irreversible $M(T)$ curves. Additionally, in several publications small values of the penetration field were obtained [204, 210, 211], but attributed to the breaking of intergranular coupling. Moreover, in more direct measurements of $\lambda$ [212, 213] by $\mu$SR experiments the penetration depth was found to be 480 nm for K$_3$C$_{60}$ and 420 nm for Rb$_3$C$_{60}$, which leads to $\mu_0 H_{c1}(0) = 4.0$ and 4.9 mT respectively.
while from optical reflectivity measurements [214] the penetration depth for K$_3$C$_{60}$ and Rb$_3$C$_{60}$ was found to be 800 nm. All of these data compel us to undertake more detailed and careful investigations of the lower critical field in fullerenes.

![Graph showing magnetic field dependence of the trapped magnetic moment](image)

**Fig. 22.** Magnetic field dependence of the trapped magnetic moment $m_t$ at $T = 5$ K for a K$_3$C$_{60}$ single crystal. [From Ref. 182]

6. Pinning Problems

As shown in the previous sections, there is good evidence that flux lines penetrate the fullerene superconductors. Because of the three-dimensional structure of the fullerene superconductors, these lines should build up an Abrikosov vortex lattice. As we discussed before, vortices are pinned by pinning centres, i.e. various structural defects in the material. Information on what kind of structural defects act as pinning centres and on the strength of the pinning force produced by these defects is very important from both the fundamental point of view and for the applicability of these materials. However, nothing is known about structural defects in fullerene superconductors by now and, therefore, we do not have any information about the nature of pinning of magnetic flux in these substances. The only point we can make is that pinning in fullerenes is strong, based on the large hysteresis of the $M(H)$ dependence and the large differences between the ZFC and the FC curves. (Experimental data related to flux pinning in fullerene superconductors are summarised in detail in Ref. [215].)

New research has to be performed on samples of good quality with known structural features and structural defects to provide us with this very important information on fullerene superconductors.
7. Conclusions

In the present contribution we discussed some experimental results on structural and magnetic properties of pure fullerenes as well as of some intercalated ones, including those which exhibit superconductivity. All of these compounds show a number of transitions both of the solid state and the magnetic phases. Though many unusual and interesting phenomena have been discovered, many fundamental questions remain unsolved. For instance, why do higher fullerenes not show ferromagnetism (intercalated by TDAE) and superconductivity (intercalated by alkali, alkali-earth or rare-earth metals)? What is the nature of the magnetism in TDAE-C$_{60}$? What is the mechanism of superconductivity in the fullerenes? Although superconductivity should be related to some kind of electron pairing, details of the pairing mechanism are not well established [34].

There are some further open questions on the superconducting properties of fullerenes. One of them is their instability in air. It is enough to expose the material to air for a fraction of a second to completely destroy superconductivity. We believe that one of the most important goals at the moment is to overcome this barrier.

While the development of sample preparation techniques is very rapid, a well developed procedure to prepare crystalline samples of good quality is still lacking. The lattice of pure C$_{60}$ crystals is usually damaged during doping and a mosaic structure appears. This mosaic structure, in addition to all other structural defects, can strongly affect flux pinning. Moreover, there is almost no information on point defects, vacancies in alkali metal or fullerene sublattices, twin boundaries, etc. in pure C$_{60}$ crystals or in intercalated ones.

The effect of granularity in powdered samples and the possible granularity of bulk crystals [203, 217] represent a central problem at present because one needs to know whether the parameters obtained from experiment are characteristic of the bulk material or of weak links, in order to establish the intrinsic superconducting parameters of these new superconductors. We believe that with the increasing quality of single crystals, significant progress towards a better understanding of the mixed state properties lies immediately ahead, and that magnetisation measurements and their comparison with other techniques will play a key role in this development.

In addition, it will be worthwhile to search for superconductivity in the polymeric AC$_{60}$ compounds, for instance in KC$_{60}$, which remains metallic down to very low temperatures.

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