SUPERCONDUCTIVITY IN ALKALI FULLERIDES

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Abstract: Superconductivity in A$_3$C$_{60}$ alkali metal fullerides occurs at moderately high temperatures, with critical temperatures $T_c$ higher than 30 K. The high symmetry of C$_{60}$ and the molecular character of the solid simplifies the description of its electronic and vibrational structure. However, these attributes introduce two characteristic energy scales in the description of the electronic and vibrational structure: one for intra-molecular processes and another for inter-molecular processes. The inter-molecular electronic energies are of the same order of magnitude as the intra-molecular vibrations and as the effective electron-electron interactions. This leads to a situation where the on-Fermi-sphere approximation is not valid, the Migdal theorem may not be applicable, and the superconductivity occurs near a metal–insulator transition. This situation for a system that has a simple underlying electronic structure makes it very interesting to study superconductivity at the limits of validity of the usual theories.

1. INTRODUCTION

From its first observation in molecular beams [1] to its synthesis in macroscopic quantities [2], C$_{60}$ remained a chemical curiosity, the molecule made of a single element supposed to have the highest symmetry, with all sixty carbon atoms occupying equivalent positions. Soon after its synthesis the icosahedral
symmetry and soccer-ball shape was confirmed. There was a huge interest in the new form of crystalline carbon, leading to the measurement of its main properties and the discovery of superconductivity at moderately high temperatures (higher than in any inter-metallic) in the $A_3C_{60}$ alkali fullerenes [3].

An excellent comprehensive review of the properties of $C_{60}$ and its compounds has been recently published [4]. We will present here a few points that are related to the moderately high values of the superconducting transition temperature $T_c$ and make the system very interesting for the study of superconductivity in real materials: the occurrence of superconductivity in a correlated material that may be close to the metal-insulator transition, the question of the validity of the Migdal theorem, and the possibility of studying the electron–phonon interaction in detail.

The key feature of solid $C_{60}$ and $A_3C_{60}$ is its molecular character which introduces two energy (length and time) scales in the system, for both electron and phonons, one, larger, for intra-molecular processes and another, smaller, for inter-molecular effects. We will discuss briefly how the presence of two energy scales raises interesting questions about the fundamental properties of the superconductivity in alkali fullerenes.

2. ELECTRONS IN THE NORMAL STATE

The simplest description of the one-electron states of $C_{60}$ and $A_3C_{60}$ takes into account the molecular character of $C_{60}$, the ionic character of the alkali–$C_{60}$ bond, and the hybridization of C atoms within the molecule. Being three fold coordinated, the C atoms in $C_{60}$ have a $sp^2$ hybridization like in graphite, with three $sp$ hybrids directed towards the neighbouring atoms. As the three bonds are not co-planar the fourth orbital which is in the radial direction has some $sp$ hybridization, in contrast to graphite where it has pure $p$ character. The three hybrid orbitals pointing to the C–C bonds form strong $\sigma$ and $\sigma^*$ (bonding and anti-bonding) molecular orbitals. The occupied $\sigma$ orbitals span an energy range of 16 eV and are separated by 9 eV from the empty $\sigma^*$ orbitals. The radial atomic orbital forms $\pi$-like molecular orbitals which are half occupied, with 7 eV separating the first orbital from the highest occupied molecular orbital (HOMO) which has $h_u$ symmetry and is five-fold degenerate. The symmetry of the lowest unoccupied molecular orbital (LUMO) is $t_{1u}$ (three-fold degenerate) and is 1.9 eV higher than the HOMO. In the solid, each $C_{60}$ molecular orbital interacts with the molecular orbitals of neighbouring molecules forming narrow molecular bands. The width of the band derived from the LUMO, which is occupied by the valence electrons of the alkali intercalants is $W \approx 0.4$ eV [5]. The energy spanned by the occupied molecular orbitals gives the energy scale of the intra-molecular interactions, several eV, while the width of the mini-bands of the solid, a few tenths of an eV, gives the much smaller electronic energy scale of the inter-molecular processes. In the $A_3C_{60}$ alkali fullerenes the valence electrons of the alkali atoms are transferred to the LUMO derived band which becomes half occupied [5].
For the isolated molecule, the ionization potential is 7.6 eV, the electron affinity is 2.65 eV and the second ionization potential of C_{60} is 4.4 eV [6]. This allows an estimation of the correlation parameter for the isolated molecule of \( U_m \approx 3.2 \) eV, corresponding to the shift of the HOMO level (of the neutral molecule) upon addition of one electron. Notice that this effect is mainly due to charging energies and not to subtle electronic correlations at the molecular or even atomic level. In fact calculations using the local-density-approximation of the density functional formalism which includes only a mean-field correlation give a value of 7.74 eV for the ionization potential and 2.78 eV for the electronic affinity [5] in excellent agreement with experiment. A classical metallic sphere with the radius of C_{60} (3.5 Å) has a difference between ionization potential and electronic affinity of \( \sim 4.1 \) eV, consistent with the hypothesis that the value of \( U_m \) is due to charging effects. In solid C_{60} the difference between the threshold for photoemission and inverse photoemission compared to the lowest excitation energies indicates a reduction of the correlation parameter to \( U_s \approx 1.5 \) eV, consistent with a molecule in a polarizable environment [4b]. At a first glance the ratio of conduction band width to correlation parameter \( W/U_s \) is small and the alkali fullerenes should be Mott insulators. However one has to take into account the attraction between electron and holes in neighbouring molecules. Assuming spherical charge distributions and neglecting screening the classical electrostatic energy of two spheres with unit charge and separated by 10 Å is \( J = -1.4 \) eV, indicating a possible strong renormalization of \( U_s \) to yield a smaller effective \( U \) required to explain the metallic character of the alkali fullerenes.

Some of the alkali fullerenes are metals and some insulators. A_{3}C_{60} are metals (with the exception of Cs_{3}C_{60}) and all A_{4}C_{60} are insulators. They should be close to the metal-insulator transition and in fact Cs_{3}C_{60} becomes metallic with applied pressure [7]. The high values of the measured resistivities in alkali fullerenes [8] also indicate that they should be close to a metal–insulator transition. One interesting aspect of the strong correlation in the alkali fullerenes is that considering the molecular solid as a three-dimensional assembly of zero dimensional structures, one could consider these crystals to be the true nanoscale limit of the Coulomb blockade problem [4a].

3. PHONONS

Phonons in A_{3}C_{60} can be of four types [4]: i) Vibrations of the molecules against each other (inter-molecular vibrations) with frequencies ranging from \( \hbar \omega = 0 \) to 6 meV; ii) Librational modes with frequencies of \( \hbar \omega = 1.2 \) to 2.5 meV in C_{60} and around 6 meV in A_{3}C_{60}; iii) Vibration of the alkali atoms against the C_{60} molecules which depend on the alkali mass but have energies of the order of 10 meV; iv) Vibrations of the C_{60} molecule (intra-molecular vibrations) which have energies extending from \( \hbar \omega = 30 \) to 200 meV.

While the low frequency inter-molecular vibrations have a strong dispersion with wave-vector, the high frequency intra-molecular vibrations have a
small dispersion. Once again we find two energy scales: several meV for inter-molecular phonons and tens or hundreds of meV for the intra-molecular phonons.

4. PHONON-MEDIATED SUPERCONDUCTIVITY

Although it has not yet been firmly established that the superconductivity in alkali fullerides is due to the electron–phonon interaction, there is not yet any compelling evidence that one should search for other coupling mechanisms. The moderately high transition temperatures $T_c$ can be explained by the high phonon frequencies of carbon based materials.

A popular expression for $T_c$ has been given by McMillan,

$$
T_c = \frac{\Theta_D}{1.45} \exp \left( \frac{-1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right),
$$

(1)

where $\Theta_D$ is the Debye temperature, $\lambda$ is a parameter that describes the strength of the electron phonon interaction, and $\mu^*$ is the repulsive Coulomb interaction parameter [9]. We will use it for a general discussion of the dependence of $T_c$ on phenomenological parameters in the alkali fullerides. First of all one notices that $T_c$ is proportional to the Debye temperature. With the phonon spectrum of C$_{60}$ molecules extending up to 0.2 eV (2200 K) the Debye temperature of the fullerides is much higher than for transition or simple metals, and therefore it should not be too surprising that the transition temperatures for the alkali fullerides may be higher than for the inter-metallic compounds. Second one notices that $T_c$ depends exponentially on the two parameters $\lambda$ and $\mu^*$ and therefore it is extremely sensitive to small errors in their estimation. The right order of magnitude of $T_c$ is all one can expect at present from theoretical estimates of those two parameters. One can look at Eq. 1 from another perspective: given $T_c$ and $\Theta_D$ derive a constraint on the values $\lambda$ and $\mu^*$. For A$_3$C$_{60}$ one finds that the required strength for the electron phonon interaction is $\lambda \sim 0.4$ to 1.0 (depending on the value of $\mu^*$), which is not very strong, considering that $\lambda = 0.43$ for Al and $\lambda = 1.55$ for Pb.

For most transition metals it turns out that $\mu^* \sim 0.1$. As discussed later this may not be the case for the alkali fullerides. The parameter $\lambda$ takes into account the scattering of an electron in band $m$ and with wave-vector $k$ into the band $m'$ and wave-vector $k'$ by a phonon of branch $\nu$ and wave-vector $q$

$$
\lambda = 2N(\epsilon) \sum_{q\nu} \frac{1}{\hbar \omega_{q\nu}} \ll \left| g(mk, m'k', q\nu) \right|^2 \gg,
$$

(2)

where $\omega_{q\nu}$ is the phonon frequency, $\ll . \gg$ denotes an average over all electron states available for scattering, and $N(\epsilon)$ is an electronic density of states. The coupling function between electrons and phonons is

$$
g(mk, m'k', q\nu) = -\sqrt{\frac{\hbar}{2M\omega_{q\nu}}} \delta_{q+k-k'}\langle \delta(\epsilon_m - \epsilon_{m'} + \hbar \omega_{q\nu}) \rangle I(mk, m'k', q\nu),
$$

(3)
where $M$ is the nuclear mass, $\epsilon_{mk}$ the electron energy, $G$ a reciprocal lattice vector, and

$$I(mk, m'k', \mathbf{q}6) = \int \psi^*_m \psi_{m'}(r) e_{\mathbf{q}6} \cdot \nabla v_{sc}(r, R^0) \psi_{mk}(r) d^3r,$$

is the matrix element with a pair of electron wave-functions $\psi$ of the gradient of the self-consistent potential with respect to the position $R^0$ of one of the atoms multiplied by the phonon polarization $e_{\mathbf{q}6}$. Equations 3 and 4 are written for a single atom per unit cell to simplify the already heavy notation, for the full expressions there are several good reviews of superconductivity in real materials [9]. The key property of $\lambda$ is that it is proportional to a density of states and to a complicated average of matrix elements between two electron wave-functions and the potential disturbance due to the motion of a single atom.

5. THE ON-FERMI-SPHERE APPROXIMATION

![Density of States](image)

Figure 1. The figure shows a typical electronic density of states (solid line) calculated for an ordered model of an alkali fulleride and for the band derived from the molecular LUMO orbital. The position of the Fermi level is indicated by the vertical solid line. The arrow indicates a possible electron-hole excitation by an intra-molecular phonon which has an energy comparable to the band width. The dashed lines show two hypothetical extreme cases for the density of states where a low electronic density of states at the Fermi level is associated with a large number of states available for scattering and a large density of states at the Fermi level is associated with no electron states available for scattering by that phonon.

In the theory of phonon mediated superconductivity one considers excitations of electrons between occupied and empty states with transfer of the
phonon energy $\hbar \omega_{ph}$ and phonon crystal-momentum $\hbar q_{ph}$. Electron properties are then supposed to change on an energy scale much larger than $\hbar \omega_{ph}$ and therefore the average in Eq. 2 over the pairs of occupied and empty states can be approximated by an integral over pairs of wave-functions on the Fermi surface and the density of states is taken at the Fermi energy $N(\epsilon_F)$.

As Fig. 1 illustrates, the highest intra-molecular phonons in alkali fullerenes have energies quite similar to the mini-band derived from the molecular $t_{1u}$ states. The precise value of $N(E_F)$ is not relevant but one has to calculate a suitable “average value” [10]. Fig. 1 shows two hypothetical situations where a high value of $N(E_F)$ is associated with a small number of states available for scattering and another where a low value of $N(E_F)$ is associated with a large number of pairs of states available for intra-molecular phonon scattering, to stress the fact that the relevant quantity is not $N(E_F)$ in the case of the alkali fullerenes.

In most A₃C₆₀ superconductors there is an orientational disorder and the electronic mean free path is small. This will wash out most structures of the density of states and therefore the number of electron states in the band divided by band-width is a reasonable measure of the effective density of states in the absence of a careful calculation.

6. VALIDITY OF THE MIGDAL “THEOREM”

Traditional estimates of the electron-phonon strength (Eq. 2-4) are based on the neglect of vertex corrections to the electron-phonon scattering, the so called Migdal theorem. Migdal’s argument is based on the smallness of the ratio of phonon to electron energy scales, $\hbar \omega_{ph}/E_F$, which is valid for most metals, but which is questionable for alkali fullerenes if one uses the inter-molecular energy scale for electrons and the intra-molecular energy scale for phonons [10,11]. The classical picture for the Migdal argument (with all the pitfalls of a classic picture of a quantum effect) is that since electrons travel much faster than phonons, a phonon emitted at site and time $(x_1, t_1)$ has a small probability of catching the electron and being absorbed at $(x_3, t_3)$ after another phonon has been absorbed or emitted at $(x_2, t_2)$ (see Fig. 2). In the A₃C₆₀ alkali fullerenes, if one uses the inter-molecular energy scale for electrons and the intra-molecular energy scale for phonons one reaches the conclusion that vertex corrections should be important and the Migdal theorem is not valid. If one looks at the left diagram in Fig. 2 and one imagines electrons and phonons propagating at comparable velocities one sees that a phonon catching up with an electron is reasonable, while if the electron propagates much faster, it is an unlikely event.

In the A₃C₆₀ alkali fullerenes the intra-molecular velocity of electrons if much faster than the intra-molecular velocity of phonons and the inter-molecular propagation of electrons if again much faster than the inter-molecular velocity of phonons. Therefore one has to develop a model with both energy
Figure 2. The diagram at left represents the traditional situation of the Migdal theorem where if an electron (straight lines) propagates much faster than the phonons (wiggly lines) the vertex correction is small because the probability of a phonon “catching” an electron is small. The “cartoon” at right shows the situation where the electron propagates fast within a molecule but “jumps” slowly from molecule to molecule. Since the fast part of the electron propagation is within a finite molecule the slow phonons can still “catch” it after it has looped around the molecule.

scales, or more precisely propagation of electrons and phonons at two velocities. In that model the electron propagates very fast within a C\textsubscript{60} molecule, but, due to its finite size, it would mainly “loop” around. As the “cartoon” on the right side of Fig. 2 shows an electron propagating fast within a molecule can be caught by a slower molecular vibration. Notice that once the electron jumps to a neighboring molecule it is very difficult to be influenced by the very slow inter-molecular phonon propagation. The possible breakdown of the Migdal theorem has to be examined taking into account the two velocity scales for both electron and phonon propagation.

7. THE VALUE OF $\mu^*$

The parameter $\mu^*$ which characterizes the residual electron-electron interaction is hard to calculate but is usually much smaller than the effective screened electron-electron repulsion $\mu$, which is of the order of unity. A popular expression relating them is [9],

$$\mu^* = \frac{\mu}{1 + \mu \log(\omega_{el}/\omega_D)}$$  \hspace{1cm} (5)

where $\omega_{el}$ is a typical electronic frequency (e.g. plasmon) and $\omega_D$ the Debye frequency. As the ratio $\omega_{el}/\omega_D$ is normally very large and the logarithmic
function varies extremely slow, the values of $\mu^*$ turn out to be very insensitive to the material, and range from 0.1 to 0.15 for most transition and simple metal superconductors. The physical picture for this renormalization is again based on the fact that electrons move much faster than the ions, which introduces a retardation effect on the attractive interaction due to the phonons: An electron traveling through the material polarizes the ions. The ions move much slower, so the polarization due to the ion motion appears when the electron that caused it has already moved away. A second electron, which decreases its energy due to the polarization of the ions, is reasonably far from the first one and their coulomb repulsion is screened by the other electrons. In other words the volume occupied by the Cooper pair contains many other electrons which can screen effectively their direct Coulomb repulsion. Notice that $\mu^*$ is used to describe the difference in the Coulomb self-energy between the normal and superconducting states, and not the self-energy itself.

A question raised for $A_3C_{60}$ alkali fullerides is which typical electronic frequency should be used in Eq. 5 to describe the screening. There are three observed plasmon frequencies, corresponding to considering 3, 63, or 243 valence electrons per $C_{60}$ (the $t_{1u}$ electrons, the $\pi$ electrons, or the $\pi$ plus $\sigma$ electrons). If one considers only the 3 $t_{1u}$ electrons then the electronic and phonon energy scales are similar and Eq. 5 predicts a very small renormalization of $\mu$, which corresponds to the absence of retardation when electronic and ionic velocities are similar. However from our discussion of the validity of Migdal's theorem one sees that the problem is not that the electron moves slowly within a molecule but that it jumps slowly from molecule to molecule. After one electron polarizes a given atom it cannot go very far in the time it takes that ion to respond, but it is certainly farther away than one would predict assuming that it always moves at its average velocity. A recent estimate [12] of the value of $\mu^*$ obtained a value of $\sim 0.4$ which is higher than the values observed in transition metals and close to the result in the absence of renormalization.

8. THE VALUE OF $\lambda$

It is possible to calculate the strength of the electron-phonon interaction parameter $\lambda$ and predict trends in the superconducting transition temperature $T_c$ [13] although the exponential in equation 1 does not allow the calculation of precise $T_c$ values. Estimates of the electron-phonon interaction $\lambda$ in the alkali fullerides using different methods and approximations put it in the range of 0.4 to 0.6 [14], which is the correct order of magnitude for a $T_c$ of 20 to 30 K if $\mu^* \approx 0.1$ but are not enough to explain $T_c$ if $\mu^* \approx 0.4$.

In many respects, alkali intercalated graphite is similar to the alkali fullerides, but the superconducting transition temperature is two orders of magnitude higher in the fullerides, corresponding to a factor of two in the value of $\lambda$ (at constant $\mu^*$). If one expands the graphite wavefunctions near the Fermi level in atomic orbitals, we can express $I(mk, m'k', q\nu)$ (Eq. 4) as a sum of
single site, two site and three site integrals. As graphite $\pi$ wavefunctions have (odd) atomic $p$ character near $E_F$, the integral with an (odd) potential gradient is zero. Furthermore the coupling of the out of plane graphite phonons with the $\pi$ wavefunctions is zero by symmetry. In the fullerides the $\pi$ orbitals of C$_{60}$ are combinations of atomic $s$-$p$ hybrids due to the curvature of the bonding network, and single site integrals do not vanish and radial vibrations couple to the electrons near $E_F$ [15]. These additional channels for electron–phonon scattering should increase the value of $\lambda$. The curvature of the covalent bonding network in C$_{60}$ may be responsible for the moderately high values of $T_c$ observed in the fullerides.

9. DEPENDENCE OF $T_c$ ON THE LATTICE CONSTANT

Experiments have shown that the superconducting transition temperature $T_c$ increases linearly with increasing lattice constant for a large family of A$_3$C$_{60}$ alkali fullerides. The lattice constant can be varied either by applying pressure or by changing the intercalants (Fig. 3). The accepted explanation is that in alkali fullerides the complicated average $\langle | g |^2 \rangle$ in equation 2 is a molecular quantity, and therefore independent of the lattice constant. The dependence of $\lambda$ on the lattice constant would be only through the density of states $N(\varepsilon)$. For a molecular crystal where near neighbour molecular interactions dominate, the shape of the band stays essentially the same, but its width decreases with increasing molecular separation. Therefore $N(\varepsilon)$ should have a simple dependence on the distance between C$_{60}$ molecules and the dependence of $T_c$ on the lattice constant should be simple. Figure 3 shows that Na$_2$CsC$_{60}$ under pressure and Na$_2$RbC$_{60}$ (with $T_c = 2.5$ K) do not follow that trend.

In most alkali fullerides, the alkali ions are a bit too large for the tetrahedral interstitial sites of the C$_{60}$ crystal. The consequence of this situation is that in the fulleride the C$_{60}$ molecules orient in such a way that the hexagons point to the small tetrahedral interstitials leaving some extra room for the ions. There are two possible ways that a C$_{60}$ molecule can do that, and most A$_3$C$_{60}$ alkali fullerides have an orientational disorder related to these two possibilities that remain at low temperatures. In Na$_2$AC$_{60}$ mixed fullerides the small sodium atoms occupying the tetrahedral interstitials leave enough room for the molecules to reorient and those crystals have an ordered low temperature phase. One can explain the two trends in the dependence of $T_c$ on the lattice constant by a different dependence of the density of states on the lattice constant for the ordered and disordered structures [13], but the breakdown of the on-Fermisphere approximation makes any argument based on $N(E_F)$ suspect. One should point out that in Eq. 3 the conservation of energy introduces a strong dependence of $g(mk, m'k', q\nu)$ on the lattice constant, since as the band-width narrows different electronic states couple with a given phonon (imagine the density of states narrowing in Fig. 1). The suggestion that $\langle | g |^2 \rangle$ was a molecular quantity rested on the assumption that for a disordered molecular system such a dependence would average out, but that may not be the case for the ordered compounds, hence a different trend of $T_c$ with lattice constant.
Figure 3. For alkali fullerides $A_3C_{60}$ there are simple trends of the superconducting transition temperature $T_c$ with lattice constant $a$. The figure shows $T_c(a)$ for Rb$_3$C$_{60}$ (squares), K$_3$C$_{60}$ (crosses) and Na$_2$CsC$_{60}$ (Xs) where the lattice constant was changed by applied pressure, and for several different compositions at zero pressure (diamonds). (Adapted from Ref. 16).

Figure 3 suggests that the obvious way to increase $T_c$ should be to increase the lattice constant. The periodic table limits us to Cs as the larger alkali intercalant (Fr is radio-active with a short life-time) and some extra space can be obtained by co-intercalating NH$_4$. There are two effects that can limit the increase of $T_c$ with lattice constant: The $t_{1u}$ derived band may become so narrow that some phonons would have energies larger than the band width and would not interact with electrons (see the narrow hypothetical density of states in Fig. 1) or the band is so narrow that one has a metal-insulator transition destroying the possibility of superconductivity. It was only recently that Cs$_3$C$_{60}$ has been synthesised [7]. It seems to be an insulator that is metallic and superconducting under pressure with $T_c$ increasing with pressure to $\sim$ 40 K at 12 GPa, that is $T_c$ decreases with increasing lattice constant. It is an interesting crystal where superconductivity can be observed near a metal-insulator transition.

10. MEASURING THE ELECTRON-PHONON INTERACTION

The phonons and valence electrons believed to be responsible for superconductivity in alkali fullerides have molecular character. It is the molecular symmetry that decides which phonons have a non-negligible interaction with the valence electrons. The LUMO orbital of C$_{60}$ has $t_{1u}$ symmetry which implies that only two (non-degenerate) $A_g$ and eight (five-fold degenerate) $H_g$ vibrational modes couple with them out of the forty-six molecular modes. The $t_{1u}$ is the vector representation of the icosahedral point group. Therefore, the
$A_g$ and $H_g$ modes are also the Raman active vibrations of C$_{60}$, which is extremely helpful for the detailed study of those vibrational modes.

The electron–phonon interaction decreases the phonon lifetime with a consequent broadening of their lines in metallic A$_3$C$_{60}$ with respect to insulating C$_{60}$ and A$_6$C$_{60}$. This broadening has been observed by Raman scattering and inelastic neutron scattering [17]. The photoemission from C$_{60}$ molecules show peaks identified as due to vibronic transitions (vibrational losses) with intensities related to the electron–vibration coupling in the molecule [18]. The coupling strengths estimated from the two sets of experiments for the coupling strength of each individual phonon mode are not in good agreement with each other, but both obtain coupling strengths for the (mostly radial) low energy $H_g$ modes that are stronger than the theoretical estimates. These seminal experiments show that it is possible to study the electron–phonon coupling in A$_3$C$_{60}$ in great detail thanks to the molecular character of the solid and the high symmetry of the molecule.

REFERENCES


