

# SUPERCONDUCTIVITY IN $M_3C_{60}$

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ABSTRACT. The general properties of  $C_{60}$  and  $M_3C_{60}$  alkali interstitial fullerenes will be briefly reviewed. We will argue that the high superconducting transition temperature observed in  $K_3C_{60}$  may be the result of the peculiar  $s$ - $p$  hybridization of the  $\pi$  electrons of  $C_{60}$  due to the curvature of its bonding network.

## 1. Introduction

The discovery that alkali fullerenes with stoichiometry  $M_3C_{60}$  have superconducting transition temperatures as high as 30 K,<sup>1</sup> the highest outside the high- $T_c$  oxide family and two orders of magnitude higher than in similar graphite intercalated compounds, raised the fundamental question of the mechanism of superconductivity in these compounds. Electron correlation in the conduction band of these compounds is expected to be strong and many of the theory for non-phonon superconductivity in correlated electron systems developed for the high- $T_c$  oxides can be adapted to the alkali fullerenes. The traditional electron-phonon coupling mechanism is however the simplest explanation for superconductivity in the alkali fullerenes.<sup>2</sup> Carbon-carbon bonds are quite strong and carbon is a light element, resulting in high vibrational frequencies, up to a value of  $h\nu = 0.2$  eV.<sup>3</sup> We have pointed out<sup>2</sup> that for an average vibrational frequency of 1100 K superconductivity could be explained in  $K_3C_{60}$  with a McMillan electron-phonon coupling parameter<sup>4</sup> of  $\lambda = 0.5$ . This is one third of the value of that parameter for Pb and slightly larger than for Al, therefore phonon mediated superconductivity in  $M_3C_{60}$  is quite plausible.

Here the main properties of  $C_{60}$  and  $M_3C_{60}$  will be reviewed on the basis of density-functional calculations of its properties.<sup>5-9</sup> Analysis of the electron-phonon matrix elements in  $C_{60}$  and graphite show that the  $s$ - $p$  hybridization of the conduction electron wavefunctions of  $K_xC_{60}$  allows for new channels for electron-phonon scattering that are not present in graphite.<sup>5</sup> This strengthens the electron-phonon interaction and explains the higher superconducting transition temperature,  $T_c$ , in the fullerenes.<sup>2,5</sup>

## 2. Properties of $M_3C_{60}$

### 2.1. BAND STRUCTURE

The electronic structure of  $C_{60}$  and  $K_3C_{60}$  has been discussed previously.<sup>6-9</sup> The agreement between the density of states calculated with the first principles local-density approximation and the shape of the experimental electron photoemission<sup>6</sup> and inverse photoemission<sup>7</sup> shows that the basic theoretical band structure is correct. Because of the weakness of the intermolecular interactions and the high symmetry of  $C_{60}$ , the electronic structure of solid  $C_{60}$  (fullerite) consists of several “minibands” associated with the molecular states. These molecular states can be characterized as being of  $\sigma$  or  $\pi$  character, and have wavefunctions with a dominant angular momentum component with respect to the center of the molecule.<sup>8,9</sup> The “almost zero-dimensional” molecular character of the solid is responsible for the sharp features observed in both the photoemission and inverse photoemission spectra.

The most important band in  $M_3C_{60}$  is the one derived from the lowest empty states of the  $C_{60}$  molecule (LUMO-states). Calculations show complete charge transfer of the K valence electron to  $C_{60}$ ,<sup>5,9</sup> and both the photoemission and inverse photoemission spectra show an half filled LUMO-derived band.<sup>2</sup> Analysis of the wavefunctions show that they are of  $\pi$  type with a nodal surface close to the  $C_{60}$  spherical surface of radius 3.5 Å, and that the dominant angular momentum is  $l = 5$  (we will call them  $\pi_5$  orbitals). The symmetry of the orbital is  $t_{1u}$ , meaning that it transforms under the symmetry operations like a vector or an atomic  $p$ -orbital. However, while the three  $p$ -orbitals of a  $t_{1u}$  representation have their maximum probability density directed along three mutually orthogonal axis, the three  $t_{1u}$  orbitals of  $\pi_5$  type have their maxima concentrated around three mutually orthogonal rings.<sup>9</sup> Considered from the tight binding or LCAO point of view, the  $\pi_5$  orbitals are derived from atomic orbitals that are almost radially oriented and have  $\sim 15\%$   $s$ - $p$  hybridization.<sup>9,10</sup> A fair approximation for the coefficients of these hybrid atomic orbitals in the molecular orbital can be obtained from the icosahedral harmonics of angular momentum  $l = 5$  that generate the same  $t_{1u}$  representation.<sup>9</sup>

Because of computational constraints, most band structures of  $C_{60}$  have been calculated for an hypothetical crystal structure with fcc lattice,  $T_h^3$  symmetry and one molecule per unit cell. The observed X-ray diffraction spectra is consistent with the presence of orientational disorder in such a structure (one can choose between two equivalent  $T_h$  molecular orientations). An important question is which features of the band structure survive the disorder. For example the necks on the second sheet of the Fermi Surface display the  $T_h$  symmetry<sup>11</sup> and may not survive the disorder. However overall the band width depends mainly on the strength of the intermolecular interactions and should be quite independent of orientational disorder. The calculated local-density band width is 0.47 eV.<sup>9</sup> The average density of states in that band is therefore 0.106 states per eV, C atom, and spin. For comparison this is half the value of the density of states at the Fermi level in aluminum.

### 2.2. PHONONS

There are four kinds of phonons in  $K_3C_{60}$ . For each  $C_{60}$  molecule there are 3 acoustic modes, 9 “optical modes” associated with the vibration of the cations with respect to the  $C_{60}$  molecule, 3 libration modes associated with rigid rotations of the  $C_{60}$  molecule, and 174

modes associated with the internal vibrations of the  $C_{60}$  molecule. Using a bulk modulus<sup>9</sup> of 18 GPa to calculate the speed of sound, and the size of the Brillouin zone, we estimate that the acoustical phonon branch extends up to  $\sim 40 \text{ cm}^{-1}$ . The modes associated with the rotation should be expected to be strongly anharmonic and have smaller force constants than the acoustic modes. In the absence of solid data about the force constants, one can only say that frequencies of a few  $\text{cm}^{-1}$  should be expected. The plasma frequency of the potassium ions in  $K_3C_{60}$  is  $74 \text{ cm}^{-1}$ . Due to screening the frequencies of the K “optical” modes should be smaller than this value. The vibrations of the  $C_{60}$  molecular cage have been calculated and measured by several authors.<sup>3</sup> They extend from 273 to  $1575 \text{ cm}^{-1}$ , and have therefore much higher frequencies than all the other modes. Also it is important to notice at this stage that there are 174 high frequency modes compared with 15 low frequency modes.

### 2.3. PLASMONS

In  $K_3C_{60}$  there are 3 electrons in the conduction band and 243 valence electrons. The corresponding (free-electron) plasma frequencies are 2.5 eV and 22 eV. The  $C_{60}$  plasmon has been observed<sup>6,7</sup> at 28 eV and at similar energies in  $K_3C_{60}$ , indicating that it is a collective mode of all the C valence electrons. The 2.5 eV is in the energy range of the expected interband optical transitions and therefore any plasmon at those energies would be severely damped.

### 2.4. ELECTRON CORRELATION

Combining the  $C_{60}$  ionization potential,<sup>12</sup>  $IP = 7.6 \text{ eV}$ , with the electronic affinity,<sup>13</sup>  $EA = 2.65 \text{ eV}$ , and the excitation gap of  $E_g \sim 1.8 \text{ eV}$  we obtain a molecular value of the electron-electron repulsion parameter  $U_{\text{bare}} = IP - EA - E_g \sim 3.3 \text{ eV}$ . In solid  $C_{60}$  this quantity will be reduced by the dielectric constant of the medium, and would be even smaller for  $K_3C_{60}$  crystals. Any reasonable renormalization of the value of  $U_{\text{bare}}$  will yield a value of the effective  $U$  that is of the order of magnitude as the width of the conduction band (a few tenths of an eV). This means that the system may be close to a metal-insulator transition and that a three-band three-dimensional Hubbard model is a possible model for the correlation effects in the conduction band of  $K_3C_{60}$ .

### 2.5. POSSIBLE MECHANISMS FOR SUPERCONDUCTIVITY

We can broadly classify the mechanisms for superconductivity proposed so far into three types: *i*) Non-phonon mechanisms that rely on the strong electron correlation in a relatively narrow band. *ii*) Electron-phonon coupling to the low frequency vibration modes of the alkali atoms or to the acoustic modes. *iii*) Electron-phonon coupling to the high frequency vibrational modes of the  $C_{60}$  molecule. The first type of mechanisms are derived from the theoretical efforts to understand the high- $T_c$  cuprates and will not be reviewed here. In the second type of mechanism the ratio of the critical temperature to typical vibration energy,  $k_B T_c / \hbar \omega_{\text{vib}}$ , is of the order of unity, and therefore requires a very strong electron-phonon interaction. One interesting physical idea in this context, is that while in common metals the perturbations in the effective electron potential due to the displacements of the charged ions are screened by the valence electrons, in  $K_3C_{60}$  there are no valence electrons

around the  $K^+$  ions and therefore its ionic potential is not well screened. The enhanced coupling between the valence electrons and the vibrations of the K ions would be due to this absence of screening electrons around the ion. The third type of mechanism requires “garden-variety” electron-phonon coupling and it will be discussed in the next section.

### 3. Electron-Phonon Coupling and Superconductivity in $K_3C_{60}$

The superconducting transition temperature  $T_c$  of a material can be estimated from the (logarithmic) average phonon frequency  $\omega_{\log}$ , the strength  $\lambda$  of the electron-phonon interaction, and the effective coulomb interaction parameter,  $\mu^*$ , using the Allen and Dynes<sup>14</sup> version of the McMillan<sup>4</sup> equation,

$$T_c = \frac{\hbar\omega_{\log}}{1.20k_B} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right), \quad (1)$$

which gives good approximate solutions to the Eliashberg equations, for  $\lambda < 1.5$ . For most metals<sup>14</sup> it has been found that  $\mu^* \approx 0.1$ , and Equation 1 can be used to estimate  $\lambda$  when  $T_c$  and the vibrational spectrum of a material are known.

The vibrational spectrum of the  $C_{60}$  molecule has been calculated by several authors using empirical force constants.<sup>15</sup> The logarithmic average of the calculated vibrational frequencies are in the 830 to 870  $\text{cm}^{-1}$  range. Considering that those calculations tend to overestimate the observed vibrational frequencies,<sup>2</sup> and that the solid should contain additional low frequency modes associated with the K ions and the translational and rotational degrees of freedom of  $C_{60}$ , we estimate that  $\hbar\omega_{\log}/k_B \simeq 1100$  K. Using this value,  $\mu^* \simeq 0.1$  and the observed  $T_c = 18$  K, equation 1 gives  $\lambda = 0.5$  for  $K_3C_{60}$ . Using reasonable estimates for the range of  $\omega_{\log}$  and  $\mu^*$  we obtain  $\lambda$  values between 0.45 and 0.8. The electron-phonon interaction is therefore reasonably strong in the potassium fulleride crystals.

Carbon has a strong scattering potential, and it should be an effective electron-phonon scatterer, in particular if we take into account the local field effects in the covalent carbon bonds. It should be no surprise that a metallic form of carbon has a strong electron-phonon coupling parameter. However graphite intercalated compounds have small values of  $T_c$ , in the 0.12 to 0.15 K range<sup>16</sup> for  $KC_8$ ,  $RbC_8$ , and  $CsC_8$ , corresponding to values of  $\lambda \approx 0.23$ . Even these values can only be explained by assuming scattering between graphite  $\pi$  states and electron state associated with the intercalated atoms.<sup>17</sup> For  $LiC_6$  where there are no Li states near the Fermi level superconductivity has not been observed down to 0.1 K, and  $\lambda$  would be even smaller.

The microscopic expression for the electron-phonon interaction parameter in a crystal is,<sup>18</sup>

$$\lambda = 2N(E_F) \sum_{\mathbf{q}\nu} \frac{1}{\hbar\omega_{\mathbf{q}\nu}} \ll |g(m\mathbf{k}, m'\mathbf{k}', \mathbf{q}\nu)|^2 \gg_{FS}, \quad (2)$$

where,  $N(E_F)$  is the density of states (per spin) at the Fermi level,  $\ll \dots \gg_{FS}$  represents a double average over the Fermi surface (FS), and

$$g(m\mathbf{k}, m'\mathbf{k}', \mathbf{q}\nu) = -\delta_{\mathbf{q}+\mathbf{k}-\mathbf{k}', \mathbf{G}} \sqrt{\frac{\hbar}{2N_c M \omega_{\mathbf{q}\nu} n_{at}}} \sum_{\alpha=1}^{n_{at}} \mathbf{e}_{\alpha}(\mathbf{q}\nu) \cdot \mathbf{I}_{\alpha}(m\mathbf{k}, m'\mathbf{k}') \quad (3)$$

is the matrix element for electron scattering from the state in band  $m$  with wavevector  $\mathbf{k}$  to the state in band  $m'$  with wavevector  $\mathbf{k}'$ , by the phonon mode  $\nu$  with wavevector  $\mathbf{q}$ . The phonon frequency is  $\omega_{\mathbf{q},\nu}$ , and its polarization vector for atom  $\alpha$  is  $\mathbf{e}_\alpha(\mathbf{q}\nu)$ .  $M$  is the nuclear mass,  $N_c$  is the number of unit cells in the crystal and  $n_{\text{at}}$  is the number of atoms in the unit cell. The Bloch matrix element for the scattering process is

$$I_{\alpha j}(m\mathbf{k}, m'\mathbf{k}') = N_c n_{\text{at}} \int \psi_{m'\mathbf{k}'}^*(\mathbf{r}) \frac{\partial V_{\text{sc}}(\mathbf{r})}{\partial R_{0\alpha j}} \psi_{m\mathbf{k}}(\mathbf{r}) d^3 r, \quad (4)$$

where the wavefunctions  $\psi$  are normalized to the crystal,  $V_{\text{sc}}(\mathbf{r})$  is the self-consistent potential, and  $R_{0\alpha j}$  is the  $j$ -th cartesian coordinate of atom  $\alpha$  in the unit cell at the origin. Notice that in  $\text{C}_{60}$  the maximum phonon energy is  $\approx 0.2$  eV, which is comparable with the 0.47 eV band width,<sup>9</sup> and the Fermi surface averaging of Equation 2 should be replaced by a more appropriate formula.<sup>19</sup>

In an atomic orbital basis set the integral in Equation 4 can be written as<sup>20</sup>

$$I_{\alpha j}(m\mathbf{k}, m'\mathbf{k}') = \sum_{j=1}^{N_c} e^{-i\mathbf{k}\cdot\mathbf{t}_j} \sum_{j'=1}^{N_c} e^{-i\mathbf{k}'\cdot\mathbf{t}_{j'}} \sum_{\beta=1}^{n_{\text{at}}} \sum_{\beta'=1}^{n_{\text{at}}} \sum_L \sum_{L'} n_{\text{at}} \bar{f}_{\beta L}(m\mathbf{k}) f_{\beta' L'}(m'\mathbf{k}') \times \int \phi_{L\beta}^*(\mathbf{r} - \mathbf{t}_j) \frac{\partial V_{\text{sc}}(\mathbf{r})}{\partial R_{0\alpha j}} \phi_{L'\beta'}(\mathbf{r} - \mathbf{t}_{j'}) d^3 r, \quad (5)$$

where  $\phi_{L\beta}(\mathbf{r})$  is the atomic orbital of type  $L$  at site  $\beta$ ,  $\mathbf{t}_j$  is a lattice vector, and  $f_{\beta Lm}(m\mathbf{k})$  are the coefficients of the wave function expansion. It is out of question to evaluate accurately Equations 2, 3, and 5 from first principles for a complicated crystal such as  $\text{K}_3\text{C}_{60}$ . The fact that  $T_c$  depends exponentially on  $\lambda$  (Eq. 1) makes any calculation using shape approximations or simplified hamiltonians to be qualitative. We will continue therefore our analysis with qualitative arguments. In Equation 5 only one of the atoms in the whole crystal is displaced, therefore only a few of the integrals

$$\langle L(\beta) | V_j(\alpha) | L'(\beta') \rangle = \int \phi_{L\beta}^*(\mathbf{r}) \frac{\partial V_{\text{sc}}(\mathbf{r})}{\partial R_{0\alpha j}} \phi_{L'\beta'}(\mathbf{r}) d^3 r, \quad (6)$$

have non negligible values. The huge sum over all the pairs of atomic orbitals in the crystal (Eq. 5) turns out to contain only a few important terms. The numerical coefficients in that equation are of the order of unity because  $|f| \sim 1/\sqrt{n_{\text{at}}}$ . In a tight binding approximation where we keep only one center and two center nearest neighbor integrals, we will have three types of non-zero integrals (Eq. 6). They are single site integrals with  $\alpha = \beta = \beta'$ , electron hopping integrals with  $\alpha = \beta$  and  $\beta'$  a nearest neighbor of  $\alpha$ , and the intrasite scattering at  $\beta = \beta'$  due to the atomic displacement at the nearest neighbor site  $\alpha$ . The weights of those matrix elements in the sum are of the order of unity because  $|f| \sim 1/\sqrt{n_{\text{at}}}$ . Examination of Equations 2 and 3 show that  $\lambda$  is proportional to the density of states per spin and per atom,  $N(E_F)/N_c n_{\text{at}}$ , inversely proportional to the phonon force constants,  $M\omega_{\mathbf{q}\nu}^2$ , and proportional to an average of  $|\mathbf{I}_\alpha|^2$ . (We use the normalization  $\sum_\alpha |\mathbf{e}_\alpha|^2 = 1$ .)

In intercalated graphite the electron states near the Fermi energy that are derived from the graphitic planes have  $\pi$ -character and are formed from the atomic  $p_z$  orbitals. For

these orbitals the contribution from single center scattering vanishes by symmetry, and only contributions from two center integrals due to the component of the atomic displacement parallel to the bond contribute to the electron-phonon scattering. Notice that atomic displacements perpendicular to the planes do not contribute to the electron scattering. In  $C_{60}$  if we form the three  $sp$  carbon hybrids that point in the direction of the C—C bonds we are left with a “dangling bond” orbital<sup>10</sup>  $0.284\phi_s - 0.256\phi_{p_x} + 0.924\phi_{p_z}$ , where  $x$  is the direction of the bond between hexagons, and  $xz$  is a symmetry plane. Angular decomposition of the local density wavefunctions around each atom confirm that this crude approximation is reasonable,<sup>9</sup> although the real wavefunctions are more complicated. This hybridization allows for the single-site scattering of the wavefunction, which have a large matrix element and two site scattering between the two  $p$  components.

#### 4. Discussion and Conclusions

According to our arguments, superconductivity in  $K_3C_{60}$  and  $Rb_3C_{60}$  is associated with the vibrations of the carbon cage. Superconductivity should occur for any dopant that can be introduced at concentrations of a few percent (around three dopant electrons per  $C_{60}$  molecule) and which turn the fullerite into a metal. This dopants could be interstitials like alkali atoms, atoms trapped inside the cage, or B and N substitutionals. It is crucial that this dopants give their electrons to the carbon cage and do not form localized impurity states. Experimental studies that correlate structural properties and electronic states with the occurrence of superconductivity will be extremely helpful for further theoretical work on the origins of superconductivity in these systems. When superconductivity exists the isotope effect should be observed for C but should be minimal for the dopants (if charge transfer is complete).

Because of its exponential dependence on  $\lambda$ , the dependence of  $T_c$  on dopant is difficult to predict accurately. Narrowing of the conduction band by increasing the  $C_{60}$  intermolecular distance will increase  $N(E_F)$  and consequently  $\lambda$  and  $T_c$ . This is the likely explanation of the reduction of  $T_c$  with pressure and is consistent with the dependence of  $T_c$  in composition. The highest phonon energy in  $C_{60}$  is 0.2 eV. This is comparable to the width of the conduction band. If the Fermi level is near the edge of the band, the highest energy phonons will see a reduced number of states available for scattering with detrimental effects on the superconductivity. If the band gets too narrow, superconductivity may disappear because there are no states available for scattering for the high phonon frequencies. Another danger of narrowing the band is that the system may be driven into an insulating phase, destroying again superconductivity. Since the curvature of the bonding network is smaller in  $C_{70}$ , the  $sp$  hybridization of the  $\pi$  system will be smaller and that will decrease  $T_c$ . Finally, since the conduction band of  $C_{60}$  is narrow, correlation effects are expected to be important, and the system may be near a metal-insulator transition. It would be very interesting to observe the interplay of both phenomena in the fullerenes, particularly to see if the superconducting  $T_c$  is enhanced in the proximity of the metal-insulator transition.

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