# Electron-Phonon Coupling and Superconductivity in Alkali-Intercalated C60 Solid

M. Schluter, M. Lannoo,[a] M. Needels, and G. A. Baraff

*AT&T Bell Laboratories, Murray Hill, New Jersey 07974*

D. Tománek

*Department of Physics and Astronomy and Center for Fundamental Materials Research,*
*Michigan State University, East Lansing, Michigan 48824-1116*

We propose that superconductivity in $A_3C_{60}$ ($A$ = K, Rb) with $T_c \geq 30$ K results from a favorable combination of high phonon frequencies and the existence of two different energy scales optimizing the coupling constant $\lambda = NV$. Calculations show that electron scattering $V$ is dominated by particular on-ball Jahn-Teller-type modes on the scale of the large on-ball $\pi$-hopping energy, while the density of states $N$ is controlled by the weak interball hopping energy. This factorization has several observed experimental consequences. Crucial differences to intercalated graphite explain the much smaller $T_c$ values in the graphite compounds.

Recently, superconductivity has been observed in crystalline "electron-doped" $A_3C_{60}$ "fullerite" compounds ($A$ = K, Rb, Cs), with superconducting transition temperature $T_c$ exceeding 30 K [1]. Several theoretical models have been proposed to account for this observation [2–7]. Here we report a detailed study of the electron and phonon states and the coupling between them. In particular, we carried out a comparative study of intercalated fullerite and of graphite intercalation compounds (GIC) which exhibit a significantly lower $T_c$ value ($T_c \approx 1$ K). This comparison helps us to identify possible coupling channels which could be responsible for the high $T_c$ in C60 compounds.

In our study we concentrate on $C_{60}$, neglecting the direct influence of the alkali atoms, an approximation which we will justify. We find that the coupling $V$ in C60 is dominated by on-ball modes of $H_g$ and $A_g$ symmetry. The coupling is about evenly distributed over lower frequency, predominantly radial modes and higher frequency, predominantly tangential modes. The strength of the coupling can be evaluated from Jahn-Teller-type considerations and amounts to about 40 meV per C60. The scale of this value of $V$ is set by the large on-ball $\pi$-electron hopping matrix elements. In fact, $V$ is enhanced by the finite curvature of C60 which allows for even stronger $\sigma$-hopping admixture. These results for an isolated C60 are only slightly modified ( < 10%) when C60 is placed into a weakly coupled fullerite lattice. For the electron-phonon coupling strength $\lambda$, this energy $V$ is combined with the conduction-electron density of states, the scale of which is set by the weak interball hopping. Using average values for $N(\varepsilon_F) \approx 15$ states/eV-spin-C60, estimated from band-structure calculations for fcc C60 and from a variety of experiments (see below), we obtain $\lambda \approx 0.6$, which is well within the range of what is needed for $T_c \approx 30$ K. To strengthen the argument we compare the electron-phonon coupling in fullerite with intercalated graphite. Our study shows two main differences between

these compounds: (i) The graphite modes equivalent to the lower-frequency buckling-type modes of C60 do *not* couple at all to $\pi$ electrons at the Fermi surface of graphite to first order, and (ii) the higher-frequency tangential modes couple less efficiently. This results from geometry: The finite curvature of C60 allows for finite $\sigma$-$\pi$ admixtures. As a consequence, $\lambda$ and $T_c$ are much smaller in the GIC. This leaves us with a rather unique situation in C60 where $\lambda$ is factorized into an intramolecular quantity $V$ and an intermolecular quantity $N$. Several experimental observations, to be discussed below, support this picture.

We begin our studies with a local-density-approximation- (LDA-) density-functional calculation for fcc C60 which essentially confirms what is known about the electronic structure [8]. Of importance here are the following points: (i) The conduction-band states are derived from a threefold-degenerate $t_{1u}$ level of C60 which broadens into a ~0.5-eV-wide band. (ii) The $t_{1u}$-derived conduction states are predominantly $\pi$ states, centered at the carbon atoms and pointing nearly radially outwards. There is some finite (a few percent) $s, p_\sigma$ admixture due to the finite curvature of C60. We can continue our investigation for pure fcc C60, assuming that the three alkali-metal electrons of $A_3C_{60}$ are donated into the $t_{1u}$ band. Reference to calculations by Martins and Troullier [8] for K3C60 indicates only small hybridization effects, which makes our model essentially correct.

We then proceed with a semiempirical ($s, p_x, p_y, p_z$) tight-binding (ETB) approach, the parameters of which were fitted to a large LDA data base of carbon molecules and solid structures. Details of this Hamiltonian are published elsewhere [9]. For C60 its predictions agree well with LDA results (e.g., the overall bandwidth, the density of states, and the symmetry of states near the gap). With this Hamiltonian we not only calculate band structures, but we also obtain the approximate deformation potentials for electronic states. The additional ingredient here

is a $d^{-n}$ scaling of all hopping matrix elements with interatomic distance $d$. Tests against LDA results indicate $n \approx 2$–3. Typical values for on-ball nearest-neighbor atomic deformation potentials range between $\sim 4$ eV/Å for $pp\pi$ up to $\sim 10$ eV/Å for $pp\sigma$, which includes the effects of electronic screening. Interball hopping is only approximately described in our ETB approach. To reproduce the LDA $t_{1u}$-derived bandwidth the individual interball hopping matrix elements can be appropriately scaled and become about a factor of 5 smaller than the corresponding on-ball hopping matrix elements. The corresponding deformation potentials due to interball vibrations are consequently also reduced by this factor. To calculate the electron-phonon coupling strength $V$ we can, therefore, neglect interball hopping to first order. However, the conduction-band width, the Fermi surface, and the exact shape of the density of states near $\varepsilon_F$ do depend on details of interball hopping. Because of uncertainties in the relative rotational arrangements of $C_{60}$ molecules these quantities cannot be calculated reliably at present, and we will therefore consider reasonable ranges of possible values of densities of states (see below).

To determine the vibrational modes of the system we use an extension of the simple Keating model [10]. We start with the isolated $C_{60}$ for which we use two nearest-neighbor on-ball elastic constants $\alpha, \beta$ with a bond-

stretching to bond-bending ratio ranging from 3:1 to 10:1 that covers the range appropriate for carbon. For comparison we also use the results of independent bond-charge model calculations [11]. Results for modes relevant for electron-phonon coupling will be given in Table I. The on-ball modes are distributed in a somewhat bimodal fashion. Modes with predominantly radial displacements are at the lower end of the spectrum, while the high-frequency modes are characterized by tangential displacements. There is some analogy to graphite, where the optical layer stretching modes are near 1600 cm$^{-1}$, while the buckling modes occupy the lower end of the spectrum. To test the magnitudes of interball scattering, we did add more empirical spring constants to model the ultralow-frequency librational modes in the 10-cm$^{-1}$ regime, the $C_{60}$ interball optical modes in the 100-cm$^{-1}$ regime, and the alkali optical modes in the 100-cm$^{-1}$ regime. The resulting contributions are small and will be neglected.

The dimensionless electron-phonon coupling constant used in the theory of superconductivity is given by [12]

$$\lambda = N(\varepsilon_F)V = N(\varepsilon_F)\sum_v \frac{\langle\langle I_v^2\rangle\rangle}{M\omega_v^2}, \qquad (1)$$

where the sum runs over all vibrational modes $v$ of the system, and where the double brackets denote a double Fermi-surface average over $(k,k')$ of the quantity

$$I_v^{ij}(k,k') = \sum_{\substack{\tau,l \\ \tau',l'}} c_{\tau l}^i(k)^* c_{\tau',l'}^j(k') \sum_R \mathbf{I}\{\mathbf{u}_\tau(v,q)e^{ik'R} - \mathbf{u}_{\tau'}(v,q)e^{ikR}\}\delta(k-k'-q), \qquad (2)$$

where $q = k - k'$ is the phonon wave vector. The sum over $\{\tau,l\},\{\tau',l'\}$ runs over all orbitals ($l$) and sites ($\tau$) of the electronic Hamiltonian, and $c_{\tau l}^i(k)$ are the eigenvector components for state $i$ at wave vector $k$. The vibrational eigenvectors $\mathbf{u}_\tau(v,q)$ for moving the atom $\tau$ along $\{x,y,z\}$ are multiplied by the intrinsic electron-phonon coupling matrix elements between the individual orbitals

$$\mathbf{I} \equiv \mathbf{I}_{\tau l,\tau,R+\tau'l'} = \mathbf{V}_\tau\langle\phi_l(r-\tau)|H|\phi_{l'}(r-R-\tau')\rangle, \qquad (3)$$

where the gradient is taken with regard to atom position $\tau$. The normalization $\sum_\tau^{C_{60}}|\mathbf{u}_\tau|^2 = 1$ requires that the density of states in Eq. (1) be normalized to states per eV, per spin, and per $C_{60}$ formula unit.

Because of the weak coupling between balls, we can carry out the double Fermi-surface integral in Eq. (1) analytically in the limit of $t_{inter}/t_{intra} \to 0$. $\langle\langle I_v^2\rangle\rangle$ in Eq. (1) then becomes $\frac{1}{9}\sum_{i,j}^3|I_v^{ij}(0)|^2$. This involves only on-ball electron-phonon coupling and $V$ can, therefore, be related to the Jahn-Teller problem of a negatively charged $C_{60}$ cluster, details of which are given elsewhere [13]. Group theory tells us that only fivefold-degenerate $H_g$ modes and onefold-degenerate $A_g$ modes can couple to the $t_{1u}$ electronic states. For these symmetries, the contributions to $V$ in Eq. (1) are $\frac{10}{6}E_{JT}(H_g)$ and $\frac{2}{3} \times E_{JT}(A_g)$, respectively [13], where $E_{JT}$ is the energy lowering due to distortions of $C_{60}$ induced by one added electron.

Using the ETB wave functions and the different phonon models, we calculate [14] $V \approx 40$ meV per $C_{60}$. De-

TABLE I. Experimental [15] and calculated $H_g$ and $A_g$ phonon frequencies $\omega_v$ (in cm$^{-1}$). Results are given for three different phonon models (see text). The individual mode-coupling constants $V_v$ (in meV), the total coupling strength $V$ [Eq. (1)], and the weighted (logarithmic) average phonon frequency $\omega_{log}$ (in cm$^{-1}$) [Eq. (4)] are also given [14].

| | | Bond charge (Ref. [11]) | | Keating $\beta/\alpha = 0.3$ | | Keating $\beta/\alpha = 0.1$ | |
|---|---|---|---|---|---|---|---|
| | $\omega_v^{expt}$ | $\omega_v$ | $V_v$ | $\omega_v$ | $V_v$ | $\omega_v$ | $V_v$ |
| $H_g(1)$ | 273 | 271 | 3.0 | 298 | 4.0 | 250 | 0.0 |
| $H_g(2)$ | 437 | 410 | 2.4 | 411 | 4.0 | 347 | 2.2 |
| $H_g(3)$ | 710 | 718 | 6.0 | 621 | 11.0 | 444 | 20.0 |
| $H_g(4)$ | 744 | 793 | 4.8 | 766 | 4.6 | 774 | 1.6 |
| $H_g(5)$ | 1099 | 1157 | 0.0 | 1162 | 0.0 | 1145 | 0.0 |
| $H_g(6)$ | 1250 | 1218 | 0.6 | 1226 | 0.0 | 1299 | 0.0 |
| $H_g(7)$ | 1428 | 1452 | 7.0 | 1500 | 4.2 | 1662 | 0.8 |
| $H_g(8)$ | 1575 | 1691 | 8.4 | 1718 | 10.0 | 1718 | 13.0 |
| $A_g(1)$ | 497 | 499 | 0.0 | 476 | 0.0 | 492 | 0.0 |
| $A_g(2)$ | 1469 | 1455 | 5.0 | 1452 | 5.2 | 1678 | 4.0 |
| $V$ | | | 37.2 | | 43.0 | | 41.6 |
| $\omega_{log}$ | | 995 | | 874 | | 797 | |

tailed couplings to the eight $H_g$ modes and two $A_g$ modes are given in Table I, together with the corresponding phonon frequencies. For comparison, experimental [15] Raman mode frequencies are also given. The coupling values for a given phonon model have also been tested by selective LDA frozen phonon calculations. Details will be given in a later publication. For all phonon models there is appreciable coupling both to the lower-frequency buckling modes as well as to the higher-frequency tangential modes. This is in contrast to the results of Ref. [7], where ~80% of the coupling was attributed to the two highest $H_g$ modes. The $q = k - k'$ dependence of the scattering is generally not important since the strength is given by the relatively dispersionless on-ball vibrations. For the $H_g$ Jahn-Teller modes the scattering is dominated by the interband terms (within $t_{1u}$) including $q = 0$. For the $A_g$ symmetric modes, $q = 0$ scattering is zero since it corresponds to a coherent overall shift of all electronic levels. For finite wave vector $q \neq 0$, $A_g$ mode scattering (interball) is finite, with its scale again given by the on-ball coupling.

The question of the size of $N(\varepsilon_F)$ in Eq. (1) is largely unsettled at this point. Estimates range from values of 1-2 states/eV-spin-$C_{60}$ derived from photoemission data [16], to values of ~6-20 derived from band-structure calculations [8], up to values of 10-15 and > 20 inferred from susceptibility [17] and NMR [18] data, respectively. If we assume an average value of $N(\varepsilon_F) \approx 15$, we arrive at values of $\lambda \approx 0.6$ for the electron-phonon coupling strength. The average temperature $\hbar \omega_{\log}/k_B$ appearing in McMillan's [19] formula for $T_c$,

$$T_c = \frac{\hbar \omega_{\log}}{1.2 k_B} \exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right], \qquad (4)$$

can be evaluated for each of the phonon models (see Table I) and is found to be very high, of the order of 1150 to 1450 K. This, when combined with a $\mu^* \approx 0.1$-$0.2$ [6,20], yields $T_c$ values (i.e., ranging from 5 to 35 K) within the range of the experimentally observed values of $T_c$.

In order to establish the validity of our model in view of the typical, sizable uncertainties in $\lambda$, we attempt to explain the large and qualitative difference between superconductivity in the intercalated $C_{60}$ solid and graphite intercalation compounds. Published values [21] for $N(\varepsilon_F)$ in GIC are similar to the lower range of values for $C_{60}$ (normalized per atom). The key difference is found in the electron-phonon coupling strength. Since the graphite sheets are flat, the lower-energy buckling-type modes do *not* couple in first order to the $\pi$ electrons near $\varepsilon_F$. The electron-phonon coupling in graphite is solely caused by the high-frequency optic modes, augmented by weak hybridization with intercalant orbitals and by interlayer effects. We calculate $\lambda$ using the identical procedure as for $C_{60}$ and find it to be reduced by about a factor of 5 as compared to $C_{60}$.

We conclude on the basis of these calculations that the observed superconductivity in alkali-intercalated $C_{60}$ compounds can be understood in terms of electron-phonon coupling. The main ingredients are strongly scattering on-ball modes set by the on-ball hopping energy scale, a density of states at $\varepsilon_F$ set by the low interball hopping energy scale, and a high average phonon frequency reflecting the light carbon mass combined with stiff on-ball modes. The result is a factorization of $\lambda = NV$ into interball and intraball quantities. This simple picture is beautifully confirmed by several experimental observations. First, for a given compound, $T_c$ decreases drastically with increasing pressure [22], which can be explained by the large compressibility of fullerite, leaving individual $C_{60}$ molecules and therefore $V, \hbar\omega_{\log}$ largely unchanged, but resulting in a decreased density of states $N$ with decreasing interball distance. Second, the observed [23] increase in $T_c$ with increasing alkali-intercalant size again supports the same density-of-states argument. In fact, these and the pressure experiments can be explained rather quantitatively assuming simply that $\lambda = NV$ with $N \sim t_{inter}^{-1} \sim d^n$ ($n \approx 2$-$3$) as is commonly done for $p$-electron overlaps. Then, the same values of ($\lambda, \mu^*$) needed to explain the absolute value of $T_c$ also describe the variation of $T_c$ between $K_3C_{60}$ and $Rb_2CsC_{60}$, solely on the basis of interball distance ($d$) variation [23]. A further confirmation of the picture can be found in the apparent disappearance of on-ball Raman phonon lines with metallic intercalation [24], which was first pointed out by Varma, Zaanen, and Raghavachari [7]. The strong on-ball electron-phonon coupling $V$ yields an increased phonon linewidth for selected modes, calculated by us to be of order 5%-10% of the phonon frequency which should wash out most of their spectral features. Individual widths can be extracted from Table I. For $q = 0$, only $H_g$ modes should be broadened, as is clearly seen in Raman scattering [23]. However, for finite $q$, $A_g$ modes should also be affected. This should be observable in neutron or two-photon Raman scattering experiments.

Finally, we would like to caution that the scenario developed here does not allow $T_c$ to be increased much further. One is approaching the limit where the electron kinetic energy is so small that it becomes comparable with the average phonon energy $\hbar\omega_{\log}$, and Migdal's approximation for calculating $T_c$ breaks down [25]. Furthermore, as the lattice constant of intercalated fullerite is increased, one is approaching the limit where the decreasing interball bandwidth becomes comparable with on-ball Coulomb interactions. At this point the effective one-electron picture used here breaks down and magnetic instabilities are expected to occur.

(a)Permanent address: Institut Supérieur d'Electronique du Nord, Lille, France.

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