RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 45, NUMBER 5 1 FEBRUARY 1992-I

Electron-phonon coupling strength and implications for superconductivity in alkali-metal-doped fullerenes

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(Received 18 October 1991)

A comparison between the electron-phonon coupling strength in graphite intercalation compounds and alkali-metal-doped C_{60} is considered. It is shown that the curvature of C_{60} leads to a slight reduction in the modulation of the single-site matrix element in comparison with the corresponding value in graphite. Nevertheless, the curvature of C_{60} makes it possible for electrons to couple with the low-frequency radial modes. This coupling causes the value of the dimensionless electron-phonon coupling parameter, λ, to be reasonably large. The large value of λ together with a large value of the density of states at the Fermi level readily yields a transition temperature of the order of 25 K for alkali-metal-doped C_{60} compounds.

The discovery of the C_{60} molecule with its fascinating structure,[1] followed by the ability to synthesize solid thin films of C_{60},[2] has led to a rapid increase in research activity on the fullerenes. Furthermore, the fact that, upon doping with alkali metals, C_{60} becomes superconducting at temperatures exceeding 30 K is of particular importance.[3–6] The understanding of the mechanism of superconductivity in these materials is thus also of great importance. In this work we consider the influence of the curvature of the C_{60} molecule on the strength of the electron-phonon coupling. Comparison between alkali-metal-doped C_{60} and alkali-metal graphite intercalation compounds, which also exhibit a superconducting transition,[7] is shown to be helpful in understanding the superconductivity in M_3C_{60}, M denoting an alkali-metal atom.

The electron-phonon coupling in M_3C_{60} is described in terms of a tight-binding Hamiltonian,[8] which is believed to be appropriate for the π bonds in carbon systems.[9] The tight-binding Hamiltonian, based on the assumption that the orbital on the carbon atom follows the displaced atom without any appreciable deformation,[10] can be written as

$$H = \sum_{n,n',s,s'} J(n,s;n',s') a^{\dagger}_{n,s} a_{n',s'}, \tag{1}$$

where (n,s) represents the atomic site, n denoting the unit cell and s the position of the atom within the unit cell, $a^{\dagger}_{n,s}(a_{n,s})$ is the creation (annihilation) operator for one electron in the orbital, $\phi(\mathbf{r}-\mathbf{R}_{n,s}-\mathbf{u}_{n,s})$, $\mathbf{R}_{n,s}$ being the equilibrium position of the atom at site (n,s) and $\mathbf{u}_{n,s}$ its displacement from equilibrium. The matrix element $J(n,s;n',s')$ in Eq. (1) is given by

$$J(n,s;n's') = \int \phi^*(\mathbf{r} - \mathbf{R}_{n',s'} - \mathbf{u}_{n',s'} + \mathbf{R}_{n,s} + \mathbf{u}_{n,s}) \times V(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} \tag{2}$$

and represents the interatomic matrix element of the atomic potential $V(\mathbf{r})$ between orbitals belonging to nearest-neighboring atoms.

The electron-phonon coupling is obtained by expanding $J(n,s,n',s')$ to first order in $\mathbf{u}_{n,s} - \mathbf{u}_{n',s'}$,

$$J(n,s;n',s') = J_0(n,s;n',s') + (\mathbf{u}_{n,s} - \mathbf{u}_{n',s'}) \cdot \nabla J(n,s;n',s'). \tag{3}$$

The Hamiltonian is then given by

$$H = H_0 + H_{e\text{-ph}}, \tag{4}$$

where

$$H_0 = \sum_{n,s;n',s'} J_0(n,s;n',s') a^{\dagger}_{n,s} a_{n',s'} \tag{5}$$

and

$$H_{e\text{-ph}} = \sum_{n,s;n',s'} (\mathbf{u}_{n,s} - \mathbf{u}_{n',s'}) \cdot \nabla J(n,s;n',s') a^{\dagger}_{n,s} a_{n',s'}. \tag{6}$$

The quantity $\nabla J(n,s,n',s')$ is the intrinsic electron-phonon coupling parameter, which we evaluate in this work and compare with its value in graphite and graphite intercalation compounds. Normally J depends only on the distance between neighboring atoms, and ∇J is directed along the bond between adjacent atoms,[10] causing the electron-phonon coupling to be nonvanishing only if the phonon mode involves bond-stretching atomic displacements. This is the reason that in graphite, for example, the electrons do not couple to the A_{2u} phonon mode, which corresponds to atomic displacements perpendicular to the graphite sheet, causing angle bending but no bond stretching. It is not transparent what the corresponding situation in C_{60} is, since the orbitals sticking out of the fullerene sphere are not pure p_z orbitals, in contrast to the orbitals perpendicular to the carbon sheet in graphite, which are pure p_z orbitals.

To calculate the influence of curvature on the value of ∇J in C_{60}, we start by constructing the relevant sp hybrids on carbon atoms. We choose a Cartesian coordinate system as shown in Fig. 1. The origin is placed at the equilibrium position of carbon atom 1, and the x axis is taken along a bond common to two hexagons. The y axis is taken to lie in the plane of a hexagon, and the z axis is taken perpendicular to the x and y axes. Then one can construct three hybrids directed along the three bonds. The fourth hybrid $|\phi\rangle$, which corresponds to the p_z orbital in graphite, is then uniquely determined by the requirement of the orthonormality of the hybrid wave functions. It can be shown that it is given by

$$|\phi\rangle = \alpha_0|s\rangle + \alpha_1|p_x\rangle + \alpha_2|p_y\rangle + \alpha_3|p_z\rangle, \tag{7}$$

where

$$\begin{aligned} \alpha_0 &= \left(\frac{-2\beta(1+2\beta)}{(1-4\beta)(1-\beta)}\right)^{1/2}, \\ \alpha_1 &= -\left(\frac{(1+2\beta)}{2(1-4\beta)(1-\beta)}\right)^{1/2}, \\ \alpha_2 &= -\left(\frac{(1+2\beta)(1-4\beta)}{6(1-\beta)}\right)^{1/2}, \\ \alpha_3 &= \left(\frac{(1-4\beta)}{3}\right)^{1/2}, \end{aligned} \tag{8}$$

and $\beta = \cos(108°)$.

The corresponding hybrid on atom 2, $|\phi'\rangle$, is given by

$$|\phi'\rangle = \alpha_0|s'\rangle + \alpha_1|p'_x\rangle + \alpha_2|p'_y\rangle + \alpha_3|p'_z\rangle \tag{9}$$

if the coordinate system centered at atom 2 (the primed system) is chosen as shown in Fig. 1, in which the y' axis lies in the second (primed) hexagon and normal to the x' axis. The matrix element $J(0,1;0,2)$ is then given by

$$J(0,1;0,2) = \langle\phi'|V|\phi\rangle. \tag{10}$$

The calculation of $\nabla J(0,1;0,2)$ proceeds by calculating the change in the interatomic matrix element as atom 2 is given an infinitesimal displacement in an arbitrary direction. Four different kinds of matrix elements will appear in the calculation, and they are defined by

$$\begin{aligned} V^\sigma &= -\langle p_x, 1|p_x, 2\rangle, \\ V^s &= \langle s, 1|s, 2\rangle, \\ V^{sp} &= -\langle s, 1|p_x, 2\rangle, \\ V^\pi &= \langle p_z, 1|p_z, 2\rangle, \end{aligned} \tag{11}$$

where the bond is taken along the x axis, and the four matrix elements V^σ, V^s, V^{sp}, and V^π are defined such that they are negative.

After lengthy calculations, we find the following

$$\nabla J(0,1;0,2) = \hat{\mathbf{i}}\frac{\partial}{\partial r}[\,\alpha_0^2 V^s + 2\alpha_0\alpha_1 V^{sp} + \alpha_1^2 V^\sigma + (\alpha_2^2 + \alpha_3^2)V^\pi]. \tag{12}$$

Despite the impression that the admixture of s, p_x, and p_y components would lead to an enhancement of the matrix element, and consequently an enhancement of the electron-phonon coupling,[11] it turns out that

$$\nabla J(0,1;0,2) = \hat{\mathbf{i}}\frac{\partial}{\partial r}[0.93V^\pi(r)]_{r_0}, \tag{13}$$

r_0 being the equilibrium distance between atoms 1 and 2. Equation (13) is obtained by using Harrison's d^{-2} universal scaling for interatomic matrix elements.[12] The intrinsic electron-phonon coupling strength in C_{60} is therefore $\sim$ 93% that in graphite. The curvature in C_{60} thus leads, contrary to what was previously assumed,[11] to only a slight weakening of the single-site matrix element for electron-phonon coupling between the mostly p_z hybrids. Similar results are obtained if $\nabla J(0,1;0,3)$ is calculated, where atom 3 is such that the bond joining it to atom 1 is common to a hexagon and a pentagon.

It may seem strange that the inclusion of σ character into the mostly π bonding would lead to a lowering of the absolute value of the interatomic matrix element J, but the hybridization scheme is such that the p_x component of the mostly π hybrid is oriented such that its negative lobe points towards the neighboring atom. Therefore, although the absolute value of $J(0,1;0,2)$ increases as a result of the overlap of the two p_x components on neighboring atoms, it also decreases even more due to the overlap of these negative-lobe p_x components with the s components on the two atoms. The decrease, as the calculation shows, is larger than the increase by 7%.

The results obtained above indicate that in C_{60}, just as in graphite, the electrons would couple only to phonon modes involving bond stretching. Contrary to the case of graphite, however, the radial modes in C_{60} do involve bond stretching,[13,14] unlike the corresponding A_{2u} mode in graphite, which only involves angle bending. In fact, the completely radial A_g breathing mode in C_{60}, whose frequency is 492 cm^{-1}, involves only bond stretching and no angle bending.[15–17] So does also the high-frequency

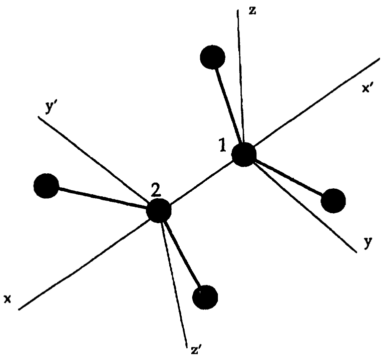

FIG. 1. A sketch of the coordinate systems used in determining the hybridization scheme for carbon atoms in C_{60}. The x, y, z coordinate system is centered at atom 1, where the x axis is directed towards atom 2, and the y axis lies in one of the two adjacent hexagons. The x', y', z' system is centered at atom 2, where the x' axis points towards 1 and the y' axis lies in the hexagon adjacent to the one in which the y axis lies.

tangential A_g mode at ~1469 cm^{-1} in C$_{60}$. These two modes are then expected to be strongly coupled to electrons in M_3C$_{60}$. Furthermore, the low frequency H_g radial modes as well as the high frequency H_g tangential modes are also expected to couple strongly to electrons in view of the bond stretching involved in these modes.

The dimensionless electron-phonon coupling parameter, λ, which appears in the McMillan formula[18] is obtained from the electron-phonon coupling matrix element $g_{kq}^{\nu\gamma}$ defined by the relation

$$H_{e\text{-ph}} = \frac{1}{\sqrt{V}} \sum_{k,q,\nu,\gamma} g_{kq}^{\nu\gamma} c_{k+q}^{\dagger} c_k (b_{q\nu\gamma} + b_{-q\nu\gamma}^{\dagger}), \tag{14}$$

where V is the volume of the crystal, $c_k^{\dagger}(c_k)$ is the creation (annihilation) operator for an electron with wave vector $\mathbf{k}$ and spin σ, and $b_{q\nu\gamma}^{\dagger}$ $(b_{q\nu\gamma})$ is the creation (annihilation) operator for a phonon with wave vector $\mathbf{q}$, branch ν, polarization γ, and frequency $\omega_{q,\nu}$. Ignoring the coupling between C$_{60}$ molecules, we obtain

$$g_{kq}^{\nu\gamma} = \left(\frac{\hbar}{2\rho\omega_{q\nu}}\right)^{1/2} I_{kk'}^{\nu\gamma}, \tag{15}$$

where

$$I_{kk'}^{\nu\gamma} = \frac{1}{2} \sum_{s,s'} \boldsymbol{\epsilon}_{q,\nu}^{\gamma} \cdot \boldsymbol{\nabla} J(0,s;0,s')(e^{i\mathbf{q}\cdot\mathbf{d}_s} - e^{i\mathbf{q}\cdot\mathbf{d}_{s'}}) U_s^* U_{s'}, \tag{16}$$

which is independent of k. Here $\boldsymbol{\epsilon}_{q,\nu}^{\gamma}$ is the phonon polarization vector, normalized to unity, $\mathbf{k}' = \mathbf{k} + \mathbf{q}$, ρ is the density of the M_3C$_{60}$ solid, $\mathbf{d}_s$ is the vector position of the atom at site s within the unit cell. The sum in Eq. (16) over s extends from 1 to 60, while the sum over s' extends from 1 to 3, and the factor of $\frac{1}{2}$ is needed to prevent double counting. U is the normalized eigenvector of the electronic Hamiltonian that corresponds to the molecular state of C$_{60}$, which would widen into the energy band under consideration.[19] These eigenvectors are real and are obtained in the limit of vanishing interball coupling by diagonalizing a 60 x 60 matrix, which is zero except for three entries of 1 in each row.

Defining $\hat{\mathbf{d}}_{ss'} = (\mathbf{d}_{s'} - \mathbf{d}_s)/|\mathbf{d}_{s'} - \mathbf{d}_s|$, $a = |\mathbf{d}_{s'} - \mathbf{d}_s|$, and $\hat{\mathbf{q}} = \mathbf{q}/|\mathbf{q}|$, we can write

$$e^{i\mathbf{q}\cdot\mathbf{d}_s} - e^{i\mathbf{q}\cdot\mathbf{d}_{s'}} \simeq qae^{i\mathbf{q}\cdot\mathbf{d}_s}(i\hat{\mathbf{q}} \cdot \hat{\mathbf{d}}_{s,s'}), \tag{17}$$

which is a valid approximation, since $qa \ll 1$ because a is much smaller than the lattice vector of the fcc lattice. Thus we have

$$\sum_{\gamma} |I_{kk'}^{\nu\gamma}|^2 = \left(\frac{0.93V^{\pi}(r_0)aq_0q}{2}\right)^2 \sum_{r,r';s,s';\gamma} (\hat{\boldsymbol{\epsilon}}_{q\nu}^{\gamma} \cdot \hat{\mathbf{a}}_{rr'})(\hat{\boldsymbol{\epsilon}}_{q\nu}^{\gamma} \cdot \hat{\mathbf{a}}_{ss'}) e^{i\mathbf{q}\cdot(\mathbf{d}_s - \mathbf{d}_r)} (\hat{\mathbf{q}} \cdot \hat{\mathbf{a}}_{rr'})(\hat{\mathbf{q}} \cdot \hat{\mathbf{a}}_{ss'}) U_s U_{s'} U_r U_{r'}. \tag{18}$$

The terms in the summation are negligible unless $s = r$ and $s' = r'$, for which case we have

$$\sum_{\gamma} (\hat{\boldsymbol{\epsilon}}_{q\nu}^{\gamma} \cdot \hat{\mathbf{a}}_{rr'})(\hat{\boldsymbol{\epsilon}}_{q\nu}^{\gamma} \cdot \hat{\mathbf{a}}_{ss'}) = 1 \tag{19}$$

and

$$\sum_{s,s'} (\hat{\mathbf{q}} \cdot \hat{\mathbf{a}}_{rr'})(\hat{\mathbf{q}} \cdot \hat{\mathbf{a}}_{ss'}) U_s^2 U_{s'}^2 \simeq \langle U^2 \rangle^2 \sum_{s,s'} (\hat{\mathbf{q}} \cdot \hat{\mathbf{a}}_{ss'})^2 \tag{20}$$

where $\langle U^2 \rangle = 1/60$. The summation over s' extends from 1 to 3, while the summation over s, which extends from 1 to 60, can be replaced by averaging $\cos^2 \eta$, η being the angle between $\hat{\mathbf{q}}$ and $\hat{\mathbf{a}}_{ss'}$, over a sphere,

$$\sum_{s,s'} (\hat{\mathbf{q}} \cdot \hat{\mathbf{a}}_{s,s'})^2 \simeq \frac{180}{\pi} \int_0^{\pi} \cos^2 \eta \, d\eta = 90. \tag{21}$$

In order to calculate the dimensionless electron-phonon coupling parameter λ we still need to double average $\sum_{\gamma} |I_{k,k'}^{\nu\gamma}|^2$ over the Fermi surface. Noting that

$$\langle\langle q^2 \rangle\rangle = \frac{\int d\sigma \int d\sigma' (\mathbf{k}' - \mathbf{k})^2 v_F'^{-1} v_F^{-1}}{\int d\sigma \int d\sigma' v_F'^{-1} v_F^{-1}}, \tag{22}$$

where $d\sigma$ and $d\sigma'$ are elements of the Fermi surface, v_F and v_F' are the corresponding Fermi velocities. Assuming that the Fermi surface is spherical, we obtain

$$\langle\langle q^2 \rangle\rangle = 2k_F^2, \tag{23}$$

k_F being the Fermi wave vector. The coupling constant λ is then given by

$$\lambda = N(E_F)Z, \tag{24}$$

where

$$Z = 3\left(\frac{0.93V^{\pi}(r_0)\, aq_0k_F}{2}\right)^2 \sum_{\nu} \frac{1}{M\omega_{\nu}^2}. \tag{25}$$

Here $N(E_F)$ is the density of states per spin per C$_{60}$ unit and M is the mass of a C$_{60}$ molecule. If the d^{-2} scaling for interatomic matrix elements is adopted, then $q_0a = 2$. The value of $V^{\pi}(r_0)$ in C$_{60}$ can be taken to be the same as in graphite, which is 2.4 eV.[20,21] The Fermi wave vector k_F can be calculated by assuming that the Fermi surface is spherical and that the charge transfer from the alkali atoms to the C$_{60}$ molecules is complete, resulting in exactly one electron per energy band. We then find that $k_F = 0.35$ Å^{-1}.

The electrons in the energy bands, which are derived from the triply degenerate F_{1u} state in C$_{60}$ couple to A_g and H_g phonon modes. Most of the contributions to λ come from the low-frequency radial modes in the range 273–770 cm^{-1}. They contribute ~65 meV to Z, while the higher-frequency tangential modes contribute ~10 meV. The value of $N(E_F)$ is uncertain, but extended Hückel band-structure calculations[22] give a value of about 20 states/eV per spin per C$_{60}$ unit. It is, however, noted[22] that this calculation may overestimate $N(E_F)$ by ~50%.

Thus if, $N(E_F)$ is taken as 12 states/eV per spin per C_{60} unit, then a value of $\lambda = 0.9$ is obtained. We then estimate T_c using the McMillan formula[18]

$$T_c = \frac{\Theta_D}{1.45} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right), \qquad (26)$$

where $\mu^* = 0.1$, $\lambda = 0.9$, and the Debye temperature $\Theta_D \simeq 500$ K, which corresponds to an average frequency of 350 cm^{-1} characteristic of the phonon frequencies in the range 270–770 cm^{-1}, thus yielding $T_c \simeq 30$K.

In conclusion, we have shown that the curvature of C_{60} leads to a slight decrease in the intrinsic electron-phonon interaction ∇J, relative to that of graphite. The larger T_c in alkali-metal-doped C_{60} relative to heavily doped graphite intercalation compounds, such as C_3K for which T_c=3 K, essentially results from the fact that electrons in M_3C_{60} can couple strongly to the low-lying A_g and H_g radial modes. The planar structure of graphite causes the coupling between the corresponding out-of-plane mode A_{2u} and the graphite π electrons to vanish.

The model presented here also is consistent with an increase in T_c as the separation between the fullerenes increases due to selection of the alkali metal dopant. Increasing the separation between fullerenes does not reduce the intrinsic electron-phonon coupling in this system, since we are concerned here with the modulation of the overlap matrix element for two neighboring atoms in the fullerene. However, the quantity Z, given by Eq. (25) is slightly reduced because of the slight reduction in k_F. In contrast, the electronic density of states increases due to the narrowing of the bands, which results from the decreased coupling between fullerenes. The net effect is an increase in the value of λ, and consequently an increase in T_c, as the separation between balls increases, in agreement with experiment.[22]

ACKNOWLEDGMENTS

The authors gratefully acknowledge Dr. G. Dresselhaus, Dr. P.C. Eklund, and Dr. R. Saito for stimulating discussions. This research was supported in part by the NSF under Grant No. DMR-88-19896.

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