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Mechanism of superconductivity in K_3C_{60}

(alkali/Buckminsterfullerene/electron–phonon coupling)

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ABSTRACT **Using electronic states and phonon states from the first-principles calculations and including both conventional electron–phonon charge coupling and Jahn–Teller coupling, we predict T_c and other superconducting properties. The only adjustable parameter in the theory is the screening length, R_{sc}. Using R_{sc} = 0.8–1.0 Å, we find excellent agreement with experiment for T_c (16–18 K), pressure dependence of T_c (ΔT_c = −6 to −10 K for 1 GPa), and ^{12}C to ^{13}C isotope shift (α_C = 0.2); experimental values: 19 K, −7 K, and 0.3, respectively.**

A number of superconducting alkali compounds of C_{60} (M_3C_{60}) have been synthesized (1–5), leading to transition temperatures T_c from 2.5 K to 33 K. Several quite different mechanisms (6–12) have been proposed to explain the superconductivity in these materials.

A suggestion by Lannoo *et al.* (6, 7), Johnson *et al.* (8) and Varma *et al.* (9) is that dynamic Jahn–Teller (JT) coupling involving high-frequency intramolecular vibrations strongly scatter electrons near the Fermi surface, leading to superconductivity. On the other hand, Zhang *et al.* (10) estimated various contributions to the electron–electron interaction in K_3C_{60} and argued that the K^+ optical-phonon modes induce a strong attraction that is the main source of superconductivity. In addition to phonon-mediated electron-pairing mechanisms, Chakravarty *et al.* (11) and Baskaran and Tosatti (12) argue that two electrons may pair by electron–electron exchange and correlation on a single C_{60} molecule.

Hamiltonian and Electron–Phonon Couplings

We present here a first-principles, quantitative study of the superconductivity K_3C_{60}, using the Hamiltonian equation

$$H = H_{ph} + H_e + H_{ee} + H^Q_{eph} + H^{JT}_{eph}, \quad [1]$$

where each term is defined below.

Phonon States (H_{ph}). We started with the graphite force field (GraFF) developed by Guo *et al.* (13) for describing the structure, elastic constants, and phonons of graphite and intercalated graphite. Without adjustments, the GraFF leads to an excellent description of the vibrational levels of C_{60} (4% average absolute error for A_g and H_g). The lattice constants of K_3C_{60} are within 0.1 Å of experiment (14, 15), and the predicted linear compressibilities (13) of K_3C_{60}, $\beta = 1.13 \times 10^{-3}$ kbar^{-1}, is close to experiment (15), $1.20(9) \times 10^{-3}$ kbar^{-1}.

Using the predicted structure of fcc K_3C_{60} [a = 14.18 Å, experimental (14, 15) a = 14.24 Å], we calculated the 189 phonon modes (eigenvectors and frequencies) for each point of a 6 × 6 × 6 grid in the Brillouin zone. These modes partition into 174 high-frequency intramolecular bands (260–1520 cm^{-1}) plus six lattice modes (130–140 cm^{-1}) involving tetrahedral K, three lattice modes (20–50 cm^{-1}) involving octahedral K, three C_{60} librational modes (30–40 cm^{-1}), and three acoustic phonon modes. We write H_{ph} as

$$H_{ph} = \sum_{k,j} \Omega_{kj}\, a^+_{kj} a_{kj}, \quad [2]$$

where Ω_{kj} is the frequency of mode j (j = 1189) with momentum $\mathbf{k}$.

Electronic States (H_e). For H_e we fitted the local density approximation (LDA) description of the conduction band by Erwin and Pickett (16) to a tight-binding Hamiltonian

$$H_e = \sum_{i,j}^{nn} t^{(1)}_{ij} c^+_{mi} c_{nj} + \sum_{k}^{nnn} t^{(2)}_{k} c^+_{mk} c_{lk}, \quad [3]$$

with the nearest (*nn*) and the next-nearest neighbor (*nnn*) hopping matrix elements. This leads to a density of states of $N(0)$ = 11.5 [the units of $N(0)$ are states per eV per C_{60}] and a Fermi energy of E_f = 0.23 eV. These compare well with the LDA results (16) of $N(0)$ = 13.2 and E_f = 0.26 eV.

We determined the Fermi surface by calculating the states from H_e at 1,000,000 points in the Brillouin zone, evaluating the Fermi energy, and selecting 330 points within 0.001 eV of the Fermi energy.

Dynamic Charge Coupling (H^Q_{eph}). Dynamic charge coupling describes the changes in the electron–ion coulomb interactions, due to vibrations (for fixed electronic orbitals). We calculated the electron–phonon coupling matrix $M_{\mathbf{k}'\mathbf{k}j}$, using the exact phonon eigenvectors and eigenenergies with a local Wannier orbital representation for the conduction electrons.

The charge-coupling Hamiltonian is written as

$$H^Q_{eph} = \sum_l \sum_{n\alpha} \Delta\mathbf{R}_{n\alpha} \cdot \nabla_{n\alpha} V_{ei}(\mathbf{r}_l - \mathbf{R}^{(0)}_{n\alpha}), \quad [4]$$

where $V_{ei}(r) = \exp(-r/R_{sc})/r$ is the screened electron–ion coulomb interaction with screening length R_{sc}, $\mathbf{R}^{(0)}_{n\alpha}$ is the equilibrium position of the αth ion in the nth unit cell, and $\Delta\mathbf{R}_{n\alpha}$ is its displacement,

$$\Delta\mathbf{R}_{n\alpha} = \sum_{\mathbf{k}j} \sqrt{1/NM_\alpha}\, Q(\mathbf{k}j)\xi(\alpha|\mathbf{k}j)\exp(i\mathbf{k}\cdot\mathbf{R}^{(0)}_{n\alpha}), \quad [5]$$

where $\xi(\alpha|\mathbf{k}j)$ is the phonon eigenvector of momentum $\mathbf{k}$ and mode j and $Q(\mathbf{k}j)$ is its amplitude.

Using the tight-binding picture, H^Q_{eph} simplifies to

$$H^Q_{eph} = \frac{1}{V^{1/2}} \sum_{\mathbf{k}'\mathbf{k}j} M_{\mathbf{k}'\mathbf{k}j} c^+_{\mathbf{k}'} c_{\mathbf{k}} (a^+_{-\mathbf{q}j} + a_{\mathbf{q}j}) \quad [6]$$

$$M_{\mathbf{k}'\mathbf{k}j} = -i \sum_{\mathbf{G},\alpha} \left(\frac{\hbar}{2\rho_\alpha \Omega_{\mathbf{q}j}}\right)^{1/2} e^{-i\mathbf{G}\cdot\mathbf{R}_\alpha} \hat{V}_{ei}(\mathbf{q}+\mathbf{G})\xi(\alpha|\mathbf{q}j) \cdot(\mathbf{q}+\mathbf{G}) W(\mathbf{q}+\mathbf{G};\mathbf{k}',\mathbf{k}), \quad [7]$$

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Abbreviations: LDA, local density approximation; JT, Jahn–Teller.

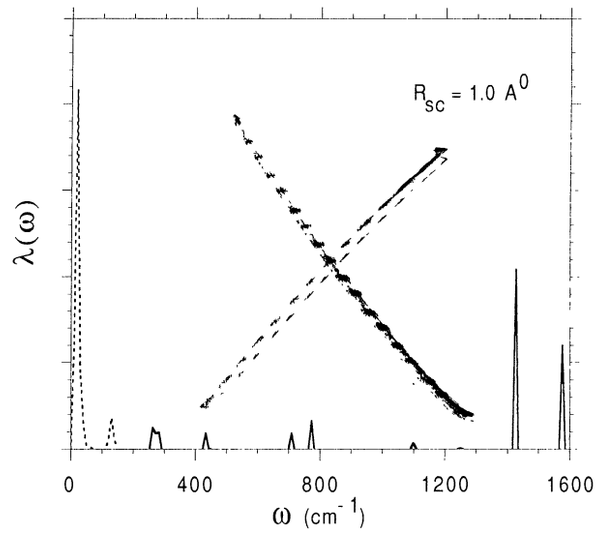

FIG. 1. Calculated values of $\lambda(\omega) = 2\alpha^2(\omega)F(\omega)/\omega$ using both Q and JT coupling; the dashed line is for $\lambda_Q(\omega)$, and the solid line is for $\lambda_{JT}(\omega)$. For $\omega < 200$ cm^{-1} all contributions are from Q, whereas for $\omega > 200$ cm^{-1} essentially all contributions are from JT. The maximum value of $\lambda(\omega)$ is 0.0669 cm.

where $W(\mathbf{q} + \mathbf{G}; \mathbf{k}',\mathbf{k}) = \Sigma_{m,n=1}^{3} A_m^*(\mathbf{k}')A_n(\mathbf{k})U_{mn}$ and $U_{mn} = \Sigma_i e^{-i\mathbf{k}'\cdot\mathbf{R}_i}\langle\psi_m(\mathbf{R}_i)|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|\psi_n(0)\rangle$. Here $\mathbf{q} = \mathbf{k}' - \mathbf{k} + \mathbf{G}$ is in the first Brillouin zone, $\mathbf{G}$ is a reciprocal lattice vector, $\mathbf{A}(\mathbf{k})$ is the electronic eigenvector of momentum $\mathbf{k}$, $\mathbf{R}_\alpha$ is the equilibrium position of the αth atom in the unit cell, ψ_m is a local Wannier wave function, and $\hat{V}_{ei}(\mathbf{q}) = 1/V_0 V_{ei}(\mathbf{q})$ (V_0 is the volume of a unit cell).

All quantities in Eqs. **4–7** were obtained directly from first-principles calculations except the screening length, R_{sc}. From Thomas–Fermi theory (17–19) an estimate is $R_{sc}^{TF} = \sqrt{E_f/6\pi e^2 n_e} = 0.63$ Å, where n_e is the conduction electron density and E_f is the Fermi energy for free electron gas. The proper value of R_{sc} for K_3C_{60} should be somewhat larger, perhaps 0.7–1.2 Å.

To calculate λ_Q, we used three p-like Gaussian functions on each C_{60} to describe approximate Wannier t_{1u} orbitals from the three electronic bands. A typical function is $\psi_x \propto x e^{-\alpha x^2 - \beta(y^2+z^2)}$, with $\alpha = 0.0397$ Å^{-2} and $\beta = 0.0550$ Å^{-2}. This treatment leads to analytic expressions for all integrals. We take the charge on each K as + electron and each C as −0.05 electron.

As indicated in Fig. 1, we find that $\lambda_Q(\omega)$ is negligible above 200 cm^{-1} and λ_Q has two peaks. One near $\omega_O \approx 20$–40 cm^{-1}, involves octahedral K plus C_{60} liberations; whereas the other at $\omega_T \approx 130$–150 cm^{-1} involves tetrahedral K.

Dynamic JT Coupling (H_{eph}^{JT}). Lannoo *et al.* (6, 7), Johnson *et al.* (8), and Varma *et al.* (9) suggested that JT coupling might play a role in the superconductivity, and Varma *et al.* (9) used modified neglect of differential overlap (MNDO) (20) calculations to estimate the couplings. We have repeated the estimates of Varma *et al.* (9) but using the vibrational modes from the GraFF (13) rather than from MNDO (20) (MNDO leads to frequencies ≈11% high). Letting g_m be the energy derivative with respect to displacement of m mode, we calculate (ref. 9 in parentheses): 0.19(0.1), 0.16(0.1), 0.26(0.2), 0.38(0.0), 0.26(0.6), 0.12(0.2), 1.77(1.8), and 1.49(1.2) for g_m of the eight H_g modes. This leads to (6–9)

$$\lambda_{JT,m} = \frac{5\,N(0)}{6\,M\omega_m^2}\,g_m^2, \qquad [8]$$

shown in Fig. 1. Thus $\lambda_{JT} = \Sigma_m \lambda_{JT,m} \sim \lambda_Q$ for $R_{sc} \approx 0.6$ to 1.0 Å.

Calculations of T_c

The Modified McMillan Equation. McMillan (21) and then Allen and Dynes (22) succeeded in developing a general formula for how the transition temperature T_c depends on the phonon density of states and the electron–phonon coupling matrix. Starting with

$$\alpha_{\mathbf{k}}^2(\omega)F_{\mathbf{k}}(\omega) = \frac{1}{(2\pi)^3}\sum_j \int \frac{d^2\mathbf{k}}{v_F}\,|M_{\mathbf{k}'\mathbf{k}j}|^2\delta(\omega - \Omega_{\mathbf{q}j})$$

$$\alpha^2(\omega)F(\omega) = \frac{1}{(2\pi)^3}\int \frac{d^2\mathbf{k}}{v_F}\,\alpha_{\mathbf{k}}^2(\omega)F_{\mathbf{k}}(\omega)\Big/\int \frac{d^2\mathbf{k}}{v_F} \qquad [9]$$

$$\lambda = \int \lambda(\omega)d\omega = 2\int \alpha^2(\omega)F(\omega)\,\frac{d\omega}{\omega}, \qquad [10]$$

where $v_F = \frac{1}{\hbar}\partial\varepsilon_k/\partial k_\perp$ is the average Fermi velocity ($k_\perp$ is perpendicular to the Fermi surface), and λ is the coupling constant. They found that (21, 22)

$$T_c = \frac{\Theta}{1.20}\exp\left[-\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right], \qquad [11]$$

where various quantities are defined in Table 1.

Results

Now defined are all quantities required to calculate the T_c from Eq. **11**. Table 2 has the calculated superconducting

Table 1. Definitions of quantities in Eq. **11**

$\Theta = f_1 f_2 \omega_{log}$	$\mu^* = N(0)V_c/[1 + N(0)V_c \log(E_e/\omega_{ph})]$
$f_1 = \left[1 + \left(\frac{\lambda}{\Lambda_1}\right)^{3/2}\right]^{1/3}$	$f_2 = 1 + \frac{\left(\sqrt{\langle\omega^2\rangle}/\omega_{log} - 1\right)\lambda^2}{\lambda^2 + \Lambda_2^2}$
$\Lambda_1 = 2.46\,(1 + 3.8\mu^*)$	$\Lambda_2 = 1.82\,(1 + 6.3\mu^*)\left(\sqrt{\langle\omega^2\rangle}/\omega_{log}\right)$
$\omega_{log} = \exp\left[\frac{2}{\lambda}\int_0^\infty \frac{d\omega}{\omega}\,\alpha^2(\omega)F(\omega)\log\omega\right]$	$\langle\omega^2\rangle = \frac{2}{\lambda}\int_0^\infty d\omega\,\alpha^2(\omega)F(\omega)\omega$

E_e and ω_{ph} are the characteristic energy of conduction electron and phonon, respectively, and $V_c = \langle 4\pi e^2/(k^2 + q_{sc}^2)\rangle$ is averaged over the Fermi surface. We take $E_e = E_\omega = 0.6$ eV (the bandwidth) and $\omega_{ph} = \omega_{log}$.

Table 2. Superconducting properties for different values of R_{sc} (the only variable in the calculations)

R_{sc} (Å)	λ_Q/λ_{JT}	μ^*	λ	T_c (K)	ΔT_c (K)†	α_C‡	α_K‡
0.50	0.17	0.29	0.90	9.7	−6.4 (−3.6)	−0.10	−0.02
0.63	0.36	0.29	1.06	11.6	−8.7 (−5.8)	0.02	0.02
0.80	0.77	0.27	1.38	16.2	−9.9 (−5.3)	0.15	0.12
1.00	1.48	0.25	1.93	17.7	−5.8 (−0.5)	0.16	0.23
2.00	7.04	0.21	6.23	20.0	−0.1 (+3.2)	−0.01	0.44
Exp.				18§, 19.3¶	−7.2‖	0.30 (6)††	

Exp., experimental results.
†Change in T_c for pressure = 1 GPa = 10 kbar; in parentheses is the change assuming $N(0) = 11.5$.
‡α is the isotope exponent ($T_c \propto M^{-\alpha}$). α_C for $^{12}C \rightarrow {}^{13}C$ and α_K for $^{39}K \rightarrow {}^{41}K$.
§Ref. 1.
¶Ref. 3.
‖Refs. 23–25.
††Ref. 26.

properties for various values of R_{sc}. These calculations use the density of states $N(0) = 11.5$ from our tight-binding calculations. The susceptibility and critical field (23) suggest that $N(0) \approx 10$–15, whereas NMR measurement (24) gives $N(0) \sim 20$. An early photoemission experiment (25) reported that $N(0) = 1.9$, which may be low due to the surface sensitivity of these experiments.

We see that $R_{sc} = 0.8$–2.0 Å leads to $T_c = 16$–20 K, in good agreement with experiment (1–3). This does not prove the Q–JT mechanism because T_c depends sensitively upon $N(0)$, but neither experiment nor theory provides a precise value. The real test must be other properties.

Superconducting K_3C_{60} leads to an unusually large drop of T_c under external pressure (26), $\Delta T_c \approx -7.2$ K for $P = 1$ GPa. Using our force field, we calculated directly the equilibrium structure (allowing buckling of the buckyballs) and phonons for $P = 1$ GPa and recalculated $\lambda(\omega)$. Here we used the LDA results (27) that $N(0)$ decreases 20% under 1-GPa external pressure. The theory leads to $\Delta T_c = -6$ to -10 K for $R_{sc} =$ 0.5 to 1.0 Å.

A second significant test is the shift of T_c with isotope substitution. Experiments lead to $\alpha_C = 0.30 \pm 0.06$ for K_3C_{60} (28) and $\alpha_C = 0.37 \pm 0.05$ for Rb_3C_{60} (29) [an early report (30) of $\alpha_C = 1.4 \pm 0.5$ may be inaccurate]. We recalculated all phonon states and $\lambda(\omega)$ for both $^{12}C \rightarrow {}^{13}C$ and for $^{39}K \rightarrow {}^{41}K$. The resulting $\alpha_C = 0.15$ and 0.16 for $R_{sc} = 0.8$ and 1.0 Å are in reasonable agreement with experiment (28–30), but R_{sc} outside this range would lead to α_C in clear disagreement with experiment. A test here would be to measure α_K, which we predict to be 0.12–0.23.

Discussion

Our conclusion is that the superconductivity of K_3C_{60} is explained quite well by the Q–JT electron–phonon coupling mechanism including both H^Q_{eph} and H^{JT}_{eph} (with $R_{sc} \approx 0.8$ to 1.0 Å). To test whether either H^Q_{eph} or H^{JT}_{eph} is sufficient, we carried out the same calculations using only one coupling.

Table 3. Effects of not having both Q coupling and JT coupling

	Q coupling			JT coupling		
R_{sc} (Å)	δT_c†	ΔT_c‡	T_c	δT_c†	ΔT_c‡	T_c
0.50	NS	NS	NS	0.20	−0.73	1.52
0.63	0.00	NS	0.00	0.02	−0.01	0.02
0.80	0.00	−0.34	0.34	0.00	0.00	0.00
1.00	0.00	−2.26	2.50	0.00	0.00	0.00
2.00	0.00	−3.56	13.12	NS	NS	NS

All quantities are in the units of K. NS indicates not superconducting.
†δT_c is the change for T_c upon $^{12}C \rightarrow {}^{13}C$.
‡ΔT_c for 1 GPa pressure.

Table 3 shows that neither H^Q_{eph} nor H^{JT}_{eph} alone accounts for the superconducting properties of K_3C_{60}. With $R_{sc} = 1.0$ Å, H^Q_{eph} leads to $T_c = 2.5$ K, which drops for smaller R_{sc}. Larger values of R_{sc} with H^Q_{eph} alone lead to higher T_c values (e.g., 13 K for $R_{sc} = 2.0$ Å) but $\alpha_C \approx 0$, in disagreement with experiment (28–30). Including only JT with $R_{sc} = 0.5$ Å leads to $T_c = 1.5$ K (which goes to zero for higher R_{sc}) and a negative value of α_C, also in disagreement with experiment (28–30); these results for JT alone differ from ref. 9 because they used a smaller, fixed value of μ^*.

The conclusion here is that synergy between H^Q_{eph} and H^{JT}_{eph} leads to the special properties of buckyball superconductors. In the range $R_{sc} = 0.8$–1.0 Å, $\lambda_Q/\lambda_{JT} \approx 0.8$–1.5, so that both contributions are comparable. With only H^Q_{eph}, T_c drops substantially because λ decreases and ω_{log} becomes very small (decreasing Θ of Eq. **11**). For only JT, λ decreases, whereas ω_{log} is very large, leading to a high μ^* and, hence, a large negative exponential term in Eq. **11** and a low T_c.

The JT coupling essential to the Q–JT mechanism is large for C_{60} because of the high symmetry. Other buckyballs (C_{70}, C_{76}) have much lower symmetry and generally do not have a degenerate ground state (first-order JT coupling) for the anion. Because eliminating JT drops T_c from ~16–18 K to ~0–3 K, we expect other buckyballs to have $T_c < 3$ K (potassium-intercalated graphite has $T_c = 0.8$ K). We do not yet have a band structure for Rb_3C_{60} to fit to Eq. **3**; however, we did a Q–JT calculation, assuming $R_{sc} = 0.8$ Å, taking Fermi surface and μ^* the same as K_3C_{60} and estimating $N(0) = 1.2 \times 11.5$ [based on the result of an LDA calculation (27)]. Using the phonon states and optimal structure for Rb_3C_{60} from our force field (13) leads to $T_c \approx 23.5$ K for Rb_3C_{60}, as compared with $T_c = 16.2$ K for K_3C_{60} [experimental values (1–3) are 29 and 19 K, respectively].

Summarizing, we find that a combination of the charge and JT electron–phonon couplings are responsible for the superconductivity in K_3C_{60}. This explains T_c, ΔT_c(1 GPa), and α_C (and predicts α_K). More definitive tests of this Q–JT mechanism will be the prediction of T_c for various mixed alkali systems (2–5) where T_c ranges from 2.5 to 33 K. There are no variables left to our disposal; thus the force fields (and hence phonons) are determined, R_{sc} must be ~ 0.8–1.0 Å, and the quantities in μ^* are defined. The only remaining variables have to do with the electronic states [e.g., $N(0)$ and Fermi surface], which will emerge from LDA calculations.

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