

Attractive Interaction and Superconductivity for K_3C_{60}

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The K^+ -ion optic phonons couple strongly to carriers on C_{60} molecules and can lead to an effective attraction at low energies. The fcc lattice is a frustrated lattice for a charge-density-wave state, opening the door to superconductivity. The competition between these instabilities is shown explicitly within mean-field theory.

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The soccerball-shaped buckminsterfullerene molecule C_{60} has attracted much attention recently. When doped with alkali atoms, it forms a metal which becomes superconducting. The transition temperatures are quite high, 18 K for potassium-doped [1] and around 28 K for rubidium-doped compounds [2,3]. The superconducting coherence length measured from critical-field experiments [4] is ~ 26 Å, only a few times the intermolecular distance, indicating a narrow band in the normal state. Holczer *et al.* [5] demonstrated that K-doped C_{60} has only a single stable superconducting phase, K_3C_{60} . Stephens *et al.* [6] reported from x-ray-diffraction data that the K_3C_{60} superconducting compound has a face-centered-cubic (fcc) structure. Little more is known about the normal or superconducting state.

In this paper, we discuss the electronic structure of K_3C_{60} , taking the doping concentration and the crystal lattice seriously. We estimate various contributions to the electron-electron interaction, and show that the K^+ -ion optical-phonon mode induces a strong attraction and should be the main source of superconductivity. If we model the system by a negative- U Hubbard model and study the competition between the charge-density-wave (CDW) and the singlet superconducting (SS) states at half filling, we find that SS is more stable than CDW since the CDW is frustrated in the fcc lattice. This explains why the doped fullerene is SS rather than CDW as in $BaBiO_3$.

To start with, consider a neutral C_{60} molecule. Among the outer four electrons of each C atom, three form strong σ bonds and are irrelevant at low temperatures. The remaining 60 π electrons are well described by a tight-binding model. The lowest unoccupied electron state is the threefold degenerate t_{1u} state, separated from the highest occupied state by a gap [7,8] ~ 2 eV. In an undoped C_{60} solid, the intermolecular interaction is a weak van der Waals interaction and the gap remains. Doping with alkali ions introduces additional electrons, and for K_3C_{60} the average valence is C_{60}^{3-} . Because the intermolecular hopping is small, we treat C_{60} as a unit. The internal degrees of freedom lead to an effective intramolecular interaction U_{eff} .

The most important issue is whether U_{eff} is repulsive or attractive. Let Φ_n be the energy of C_{60}^{n-} ion carrying n

additional electrons. Then for K_3C_{60}

$$U_{\text{eff}} = \Phi_2 + \Phi_4 - 2\Phi_3. \quad (1)$$

We estimate various contributions to U_{eff} . First there is an intramolecular Coulomb repulsion. For an isolated C_{60} , the direct Coulomb repulsion U_{e-e} of (1) is at least $1.42e^2/d$ (d is the diameter of C_{60}). This estimate from point charges on C_{60} gives $U_{e-e} \sim 2.5$ eV. In a solid, screening by the induced charge distribution on neighboring molecules reduces U_{e-e} . We estimate the screened U_{e-e} to be roughly 1.2–1.7 eV [9]. Because of this sizable repulsive U_{e-e} , it is necessary to have a strong attraction to produce a net $U_{\text{eff}} < 0$.

(i) K^+ -ion optical-phonon mode.—There are two sites for K^+ ions: $K^+(1)$ at the center of the tetrahedron consisting of four nearest-neighbor (nn) C_{60} molecules, and $K^+(2)$ at the center of every two next-neighbor C_{60} molecules which is the center of the octahedron (see Fig. 1). Consider the Einstein modes of a K^+ ion with mass M relative to its surrounding C_{60} . The frequencies of the phonon modes are $\omega_1 = (k_1/M)^{1/2}$ for $K^+(1)$ and $\omega_2 = (k_2/M)^{1/2}$ for $K^+(2)$, with k_1, k_2 being the elastic constants for K^+ in tetrahedral and octahedral sites. To calculate U_{eff} , we consider a tetrahedron consisting of one C_{60}^{4-}

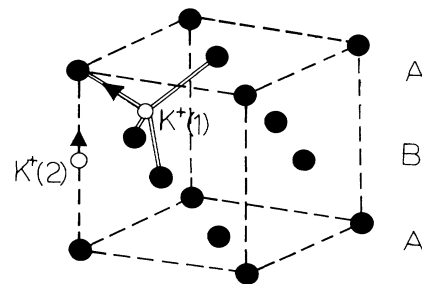


FIG. 1. The fcc lattice structure of K_3C_{60} . Solid circles represent C_{60}^{3-} molecules. They are surrounded by eight $K^+(1)$ at the center of the tetrahedron consisting of four nearest-neighbor C_{60} , and six $K^+(2)$ located at the middle of every two next-nearest-neighbor C_{60} . Only one of each is shown by an open circle. The ratio of $K^+(1)$ and $K^+(2)$ sites is 2:1. The arrows indicate K^+ motion toward the more negatively charged C_{60} . A and B represent the two sublattices for CDW consideration.

(or C_{60}^{2-}) and three C_{60}^{3-} and the $K^+(1)$ ion inside the tetrahedron moves toward (or away from) the C_{60}^{4-} (or C_{60}^{2-}). It follows that $k_1 = \frac{4}{3}k_0$, where k_0 is the spring constant of a $K^+(1)$ with respect to a single neighboring C_{60} . ω_1 (also ω_2) can be measured directly. An estimate based on the transverse optical-phonon frequency for potassium halide crystals [10] gives $k_0 = 1.3 \text{ eV/\AA}^2$, leading to $\omega_1 = 160 \text{ K}$ [11].

The energy due to the displacement x of a K^+ ion is [12], within the harmonic approximation,

$$W_1 = \frac{1}{2} k_1 x^2 - (e^2/d^2)x, \quad (2)$$

where $d_1 = \sqrt{3}a/4$ is the distance from the center to a vertex of the tetrahedron ($a = 14.24 \text{ \AA}$ is the fcc lattice constant). The optimal value of W_1 is $W_1 = -128e^4/9M\omega_1^2 a^4$. There are eight tetrahedra sharing one C_{60} . Taking account of the contribution from C_{60}^{2-} , we get $U_{\text{eff}}(K^+(1)) = 16W_1 = -0.65 \text{ eV}$. The $K^+(1)$ phonon is similar to the usual breathing mode. The attraction it generates is very strong [13].

A similar calculation is applied for the $K^+(2)$ mode, and we find $U_{\text{eff}}(K^+(2)) = -96e^4/M\omega_2^2 a^4$. Taking $\omega_2 = \omega_1$, $U_{\text{eff}}(K^+(2)) \sim -0.27 \text{ eV}$. Actually $\omega_2 < \omega_1$, since the space provided by the octahedron of six C_{60} is large enough to fit an atom of radius 2 \AA , while the radius of a K^+ ion is only 1.33 \AA . Thus the $K^+(2)$ phonon mode should be very soft.

(ii) *C-C dimerization mode.*—We adopt the polyacetylene model of Su, Schrieffer, and Heeger [14] for a single C_{60} molecule,

$$H_1 = - \sum_{(i,j)\sigma} (t_{i,j} a_{i\sigma}^\dagger a_{j\sigma} + \text{H.c.}) + \sum_{(i,j)} \frac{1}{2} k_C (u_i - u_j)^2, \quad (3)$$

where $t_{i,j} = t_0 - \alpha(u_i - u_j)$. The summation is over all the C-C bonds within one molecule. $a_{i\sigma}$ is the annihilation operator for C π electron, and u_i is the displacement of the i th carbon along the bond connecting two pentagons. t_0 is the electron hopping integral without the displacement, α the electron-phonon interaction, and k_C the C-C spring constant. The displacement is chosen as $\pm u_0$; i.e., the 60 bonds forming the pentagons are long and the other 30 bonds are short. We diagonalize H_1 numerically to find the optimal values of u_0 for C_{60}^{n-} . The parameters for the polyacetylene are used, $t_0 = 2.5 \text{ eV}$, $\alpha = 4.1 \text{ eV/\AA}$, and $k_C = 21 \text{ eV/\AA}^2$. The results are summarized in Table I. For a neutral C_{60} , we find a difference in length between long and short bonds of $3u_0 = 0.043 \text{ \AA}$, in excellent agreement with experiment,

indicating the reliability of our simple model. From the total energy, we obtain $U_{\text{eff}}(\text{dimer}) = -0.026 \text{ eV}$: only a small attraction from the relaxation of the bond lengths.

(iii) *Jahn-Teller distortion.*—This comes from the threefold degeneracy of the partially filled electron t_{1u} states. Upon doping, the C-C bond length changes breaking the degeneracy in favor of one of them. We believe this attractive U_{eff} is $\sim 10 \text{ meV}$, at most comparable to (ii).

The above discussion shows that the K^+ phonon modes are coupled most strongly. However, the use of the static limit is questionable because of the finite electron bandwidth. Estimates from band-structure calculations give values for the Fermi energy of $E_F \sim 0.2 \text{ eV}$ [8], larger than the phonon frequencies. However, if we estimate the electron-phonon coupling strength in the dynamic limit, again the K^+ phonon modes are the strongest with dimensionless coupling $\lambda = 8$ for the $K^+(1)$ phonon [using a band-structure value [8] of the density of states $N(0) = 12 \text{ states/eV}$; C_{60}]. These large values raise the question of the competition with localized or CDW states which would occur in the true static or strong-coupling limit.

We begin by addressing the competition between CDW and superconductivity (SS) in the limit of a nonretarded attractive interaction. The weak overlap of electron states on nn C_{60} molecules generates a small hopping integral of the doped electrons. In band theory, K_3C_{60} is a half-filled band. In a bipartite lattice, a negative- U model with nn hopping has degenerate CDW and SS ground states [15,16]. A natural question is what would happen for K_3C_{60} . The key point is that K_3C_{60} has a fcc structure which is frustrated with respect to charge disproportionation and the SS state is always energetically more favorable than CDW.

To obtain a detailed understanding relevant to K_3C_{60} , we study the simplified model of a single half-filled band attractive ($U < 0$) Hubbard model [17] within mean-field theory. The Hamiltonian is

$$H = -t \sum_{(i,j)\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + \text{H.c.}) + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (4)$$

where the summation is over all the nn pairs in a fcc lattice, and $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$. Consider the two sublattices A and B illustrated in Fig. 1 for the CDW state [18]. The order parameter is δ , with $\langle n_i \rangle = 1 \pm \delta$, with $+$ ($-$) for sublattice A (B). Decoupling the U term in (4), we obtain the energy per electron,

$$E_{\text{CDW}} = \frac{2}{N} \sum_{\mathbf{k},s}^{\text{occ}} \epsilon_{\text{CDW}}(\mathbf{k},s) + \frac{U}{4} (1 - \delta^2), \quad (5)$$

TABLE I. The optimal displacement u_0 and the energy change $\Delta\Phi_n$ due to the displacement of the polyacetylene model for C_{60} molecular ions, Hamiltonian H_1 of Eq. (3).

	C_{60}	C_{60}^-	C_{60}^{2-}	C_{60}^{3-}	C_{60}^{4-}	C_{60}^{5-}	C_{60}^{6-}
u_0 (\AA)	0.0145	0.0120	0.0095	0.0070	0.0045	0.0020	$< 5 \times 10^{-5}$
$\Delta\Phi_n$ (eV)	-0.4405	-0.3018	-0.1895	-0.1033	-0.0432	-0.0089	...

with

$$\begin{aligned} \epsilon_{\text{CDW}}(\mathbf{k}, s) &= \gamma_k t + s(t^2 \beta_k^2 + U^2 \delta^2/4)^{1/2}, \\ \gamma_k &= -4 \cos(k_x a/2) \cos(k_y a/2), \\ \beta_k &= -4 [\cos(k_x a/2) + \cos(k_y a/2)] \cos(k_z a/2). \end{aligned}$$

In (5), the sum is over the $N/2$ lowest-energy states (\mathbf{k}, s) , with N being the electron number. The optimal value of E_{CDW} is obtained by $\partial E_{\text{CDW}}/\partial \delta = 0$.

To study the SS, we decouple

$$n_{i\uparrow} n_{i\downarrow} = (\Delta c_{i\uparrow} c_{i\downarrow} + \text{H.c.}) + \sum_{\sigma} n_{i\sigma} / 2 - (\frac{1}{4} + \Delta^2),$$

where $\Delta = \langle c_{i\uparrow}^\dagger c_{i\downarrow}^\dagger \rangle$ is the real SS order parameter. The energy of the SS state is

$$E_{\text{SS}} = -\frac{1}{N} \sum_{\mathbf{k}} \epsilon_{\text{SS}}(\mathbf{k}) + (\frac{1}{4} - \Delta^2) U, \quad (6)$$

where $\epsilon_{\text{SS}}(\mathbf{k}) = \{(U\Delta)^2 + [\epsilon_0(\mathbf{k}) - \mu]^2\}^{1/2}$, $\epsilon_0(\mathbf{k}) = t(\gamma_k + \beta_k)$ is the band dispersion, and the sum is over the whole Brillouin zone. Δ and the chemical potential μ are given by the self-consistency equations, $\partial E_{\text{SS}}/\partial \Delta = 0$ and $\partial E_{\text{SS}}/\partial \mu = 0$.

Results for E_{CDW} and E_{SS} are shown in Fig. 2. For all $U < 0$, SS is more stable than CDW. We also find a critical value of $|U|/t$, below which a CDW is not realized. Both are consequences of the fcc lattice. Below we demonstrate these points analytically to gain further insight.

Consider the limit $|U|/t \gg 1$. Then at the zeroth order all electrons are in doubly occupied configurations to gain the potential energy $U/2$ per electron for both CDW and

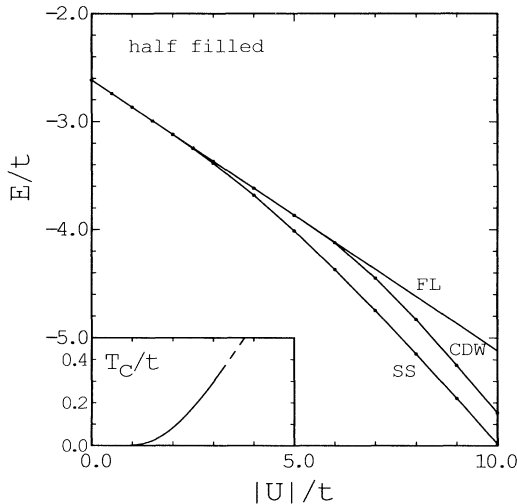


FIG. 2. Energies per electron of the $U < 0$ Hubbard model in fcc lattice at $T=0$, calculated within the Hartree-Fock approximation for the free band electron state (FL), CDW state, and superconducting state (SS). SS has lower energy than CDW in the whole parameter region. Inset: The superconducting transition temperature as a function of $|U|$.

SS. This degeneracy breaks down in a frustrated lattice at the second order in t . In an arbitrary lattice with nn coordination N_{nn} at half filling, $E_{\text{CDW}} = U/2 - N_{AB} t^2 / |U|$, $E_{\text{SS}} = U/2 - N_{\text{nn}} t^2 / |U|$, where N_{AB} is the nn coordination in the different sublattice in CDW. For a bipartite lattice, $N_{AB} = N_{\text{nn}}$, and the SS and CDW are degenerate. In a fcc lattice, $N_{\text{nn}} = 12$, but $N_{AB} = 8$, reflecting the lattice frustration. In this case, E_{CDW} and E_{SS} can be reduced from (5) and (6).

To understand the small- U region and the critical value U_c for CDW, we have calculated the charge susceptibility in the fcc lattice,

$$\chi(\mathbf{q}) = -\sum_{\mathbf{k}} (f_{\mathbf{k}} - f_{\mathbf{k}+\mathbf{q}}) / [\epsilon_0(\mathbf{k}) - \epsilon_0(\mathbf{k}+\mathbf{q})],$$

where $f_{\mathbf{k}}$ is the Fermi function. Because of the lack of nesting, there is no strong peak in \mathbf{q} space, and χ is between $0.15/t$ and $0.18/t$ at $T=0$ K in the whole \mathbf{q} space. From a simple random-phase-approximation argument, the CDW instability against the free-electron state occurs at $1 = U\chi(\mathbf{q})$, giving a critical value around $|U|/t \sim 6$, which is consistent with the Hartree calculation in Fig. 2.

The SS transition temperature T_c of the model (4) is given by

$$\frac{1}{N} \sum_{\mathbf{k}} \frac{\tanh[\epsilon_0(\mathbf{k}) - \mu] / 2k_B T_c}{2[\epsilon_0(\mathbf{k}) - \mu]} = \frac{1}{|U|}, \quad (7)$$

with μ determined by $\sum_{\mathbf{k}\sigma} f_{\mathbf{k}\sigma} / N = 1$. The results are plotted in Fig. 2. Note that this mean-field value of T_c is accurate only in the weak-coupling limit. For large values of $|U|/t$, substantial deviations are expected [19,20].

When retardation is included the CDW state will be favored but, because of the frustration in the fcc lattice discussed above and also because the ratio of electronic to phononic energy scales, $R = E_F / \omega_{\text{ph}}$, is unusually small here ($R \sim 15$), we expect that the transition to the CDW will be displaced to unusually large values of the electron-phonon coupling. The Coulomb pseudopotential which will enter the Eliashberg equations will, however, be unusually large and we estimate it as $\mu^* = N(0)U_{e-e} / [1 + N(0)U_{e-e} \ln R] \sim 0.36$, which points again to the importance of the strong coupling to the K^+ phonons.

In conclusion, we have shown in this paper that the doped-alkali-ion phonon mode produces a strong attraction for electrons on C_{60} , which is an order of magnitude larger than those induced from the C-C bond-length-alternation phonon modes, and can be strong enough to overcome the electron-electron Coulomb repulsion. We have demonstrated, using a single-band negative- U Hubbard model, the crucial role of the fcc crystal lattice in K_3C_{60} in preferring the superconducting ground state over the charge-density-wave state.

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- [9] We approximate the other C_{60} molecules by a spherical metallic cavity with radius b_1 . This cavity has surface charges which are induced by a charge on the embedded C_{60} with radius b_2 ($\sim d/2 = 3.5 \text{ \AA}$). The radius b_1 should be between 7 and 10 \AA . The effective dielectric constant ϵ thus obtained for C_{60}^{4-} is 2 and 1.5 for $b_1/b_2 = 2$ and 3, respectively.
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- [11] Similar to alkali halides, the distance between the centers of the C_{60} ion and the $K^+(1)$ is close to the sum of the ionic radii. We estimate the value of k_0 from KBr or KI with large negative ions.
- [12] In W_1 , the dielectric constant used for U_{e-e} (Ref. [9]) does not appear because the uniform charge induced on the cavity surface does not yield an electric field at the positions of $K^+(1)$ and $K^+(2)$ which are inside the cavity. Even if we consider the charge polarization on the nearest-neighbor C_{60} , we find that the coefficient of e^2x/d^2 is close to 1.
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