

Jahn–Teller effect in C_{60} molecules as a possible reason for the superconductivity of doped fullerite

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The “high-temperature” superconductivity of solid fullerene (fullerite) doped with alkali metal atoms may result from a dynamic lifting of the band degeneracy and virtual interband (or intervalley) transitions of electrons. These transitions would be caused by deformation vibrations of the highly symmetric C_{60} molecules (buckyballs) exhibiting a Jahn–Teller effect. This idea would explain, in particular, why the hyperfullerenes C_n with $n \geq 70$ do not exhibit a superconductivity in crystals: They do not have Jahn–Teller properties, because of their lower symmetry.

1. The sensational recent discovery of superconductivity with relatively high transition temperatures, $T_c \approx 20$ –40 K, in the crystalline phase of the fullerene C_{60} , i.e., fullerite, doped with atoms of the alkali metals, K, Rb, and Cs (Refs. 1 and 2; see also the review in Ref. 3), has raised the questions of the nature of this phenomenon and its relationship with the mechanism for the high- T_c superconductivity of the metal oxides, both those which do contain copper [LaBaCuO (Ref. 4), YBaCuO (Ref. 5), etc.] and those which do not (BaKBiO; Ref. 6).

The vibration spectrum of the C_{60} molecules is exceedingly rich. Correspondingly, the phonon spectrum of fullerite is also rich, extending to frequencies⁷ $\omega \approx 2 \times 10^3 \text{ cm}^{-1}$. It has been found that T_c increases with increasing radius of the dopant atom,⁸ while it decreases with increasing pressure.⁹ These two effects may be due to a corresponding change in the density of states in the conduction band, as a result of a decrease (or increase) in the degree of overlap of the π orbitals of neighboring molecules.³ All these facts suggest that the superconductivity of doped fullerite, $A_x C_{60}$

(where A is an alkali metal), is based on a Cooper pairing of conduction electrons as the result of an electron-phonon coupling, i.e., the standard BCS mechanism.¹⁰ A question which remains unclear, on the other hand, is just why there is no superconductivity (or, at best, the superconductivity is greatly suppressed) in A_xC_{70} crystals,¹¹ whose phonon spectrum is even richer.¹⁾

In this letter we suggest that the "high-temperature" superconductivity of the A_xC_{60} systems might be due to a Jahn-Teller effect, which is characteristic of specifically highly symmetric C_{60} molecules in charged ("ionic") states¹⁵ and which is accompanied by a spontaneous deformation of the buckyballs. In crystals with the stoichiometric composition A_3C_{60} , there is a dynamic lifting of the degeneracy of electron band states in the course of an interaction of the molecules with the doping electrons. This effect leads to a multivalley band structure, a substantial increase in the electron-phonon coupling, and an increase in T_c .

2. In A_3C_{60} crystals, with an fcc lattice, the threefold degeneracy of the molecular t_{1u} level, from which the states of the conduction band are constructed, is partially lifted by the overlap of π orbitals of neighboring molecules. The structure of the empty conduction band (a p band) with one extra electron is described in the strong-coupling approximation by the Hamiltonian

$$\mathcal{H}_t = \epsilon \sum_{n,\nu,\sigma} a_{n\nu\sigma}^+ a_{n\nu\sigma} + \sum_n \sum_{n',\nu,\nu',\sigma} \tilde{t}_{nn'}^{\nu\nu'} a_{n\nu\sigma}^+ a_{n'\nu'\sigma}, \quad (1)$$

where $\epsilon = E(t_{1u}) - E(h_u)$ is the energy of the intramolecular electronic transition from the h_u "ground" state to the first excited state, t_{1u} , of the C_{60} molecule; the operator $a_{n\nu\sigma}^+$ ($a_{n\nu\sigma}$) creates (annihilates) an electron with a spin σ in site n in state ν from the triplet t_{1u} ; and $\tilde{t}_{nn'}^{\nu\nu'}$ is the overlap integral for the overlap of different orbitals of molecules in neighboring sites n and n' . In general, diagonalizing Hamiltonian (1) in the \vec{k} representation is an exceedingly tedious procedure. If \vec{k} is directed along a diagonal of the Brillouin zone, on the other hand, the band spectrum of an fcc crystal simplifies to²⁾

$$\epsilon_{1,2}(\vec{k}) = \epsilon - tz\gamma(\vec{k}); \quad \epsilon_3(\vec{k}) = \epsilon + 2tz\gamma(\vec{k}), \quad (2)$$

where $t \equiv \tilde{t}_{nn'}^{\nu\nu'}$ for the case $\nu = \nu'$, z is the number of nearest neighbors, and $\gamma(\vec{k})$ is a structure vector of the lattice. At $t > 0$ the minima (valleys) with a high density of states, which lie at the L points on diagonals of the Brillouin zone, retain a partial (twofold) degeneracy, in agreement with numerical calculations.¹⁶

The interaction of the extra electron with the vibrations corresponding to a Jahn-Teller deformation of charged C_{60} molecules is described in the site representation by the Hamiltonian

$$\mathcal{H}_{int} = \sum_{\nu,\nu'} \sum_{n,\sigma} \chi_{\nu\nu'} a_{n\nu\sigma}^+ a_{n\nu'\sigma} u_n^{\nu\nu'}, \quad (3)$$

where $\chi_{\nu\nu'}$ are the interaction matrix elements, and the operators $u_n^{\nu\nu'}$ represent the normal intramolecular vibrations, which mix different states of the t_{1u} multiplet and

which, in the $A_x C_{60}$ crystal, split the conduction band and induce interband transitions. A symmetry analysis clearly shows that the intramolecular vibrations of C_{60} with h_g symmetry are Jahn–Teller vibrations.^{3,15} According to experimental data,⁷ these vibrations undergo the greatest changes (in position and also in the intensity of the lines in the spectrum of scattered neutrons) upon the transition from the insulating C_{60} crystal to the $A_x C_{60}$ metal.

3. The effective Hamiltonian of a multiband metal with bands overlapping at the Fermi level can be written as follows, on the basis of (1) and (3) (Refs. 17 and 18):

$$\begin{aligned} \mathcal{H}_{eff} = & \sum_{\vec{k}, \sigma i} [\epsilon_i(\vec{k}) - \mu] a_{\vec{k}\sigma i}^{\dagger} a_{\vec{k}\sigma i} \\ & + \sum_{i,j,l,m} \sum_{\vec{k}, \vec{k}', \vec{q}, \sigma, \sigma'} W_{ij,lm}(\vec{q}) a_{\vec{k}+\vec{q}, \sigma i}^{\dagger} a_{\vec{k}'-\vec{q}, \sigma' j} a_{\vec{k}' \sigma' n} a_{\vec{k} \sigma l}. \end{aligned} \quad (4)$$

Here μ is the chemical potential, which determines the position of the Fermi level; the operator $a_{\vec{k}\sigma i}^{\dagger}$ ($a_{\vec{k}\sigma i}$) creates (annihilates) an electron with a quasimomentum \vec{k} and a spin σ in band i ; and $W_{ij,lm}$ are the matrix elements of the intraband and interband interactions, which include the electron–phonon coupling and the electron–vibrational interaction in (3) in second-order perturbation theory (as well as the screened Coulomb repulsion).

If the Fermi level intersects the twofold-degenerate band [see (2)], whose degeneracy is lifted by the electron–phonon interaction, with a constant $\chi_{\nu\nu'}$ for $\nu \neq \nu'$ [see (3)], then we can find a system of equations for the order parameters Δ_1 and Δ_2 in the dynamically split bands as $T \rightarrow T_c$. Here we use the Gor'kov equations for the normal and anomalous Green's functions G_{ij} and F_{ij} in a two-band superconductor,^{17,18} if only the intraband pairing of carriers is taken into account.³ These equations are

$$\left. \begin{aligned} \Delta_1(1 - \Lambda_1 L) - \Delta_2 \bar{\Lambda}_{12} L &= 0 \\ \Delta_2(1 - \Lambda_2 L) - \Delta_1 \bar{\Lambda}_{12} L &= 0 \end{aligned} \right\}. \quad (5)$$

Here

$$\Lambda_i = \lambda_i + \Lambda_{12}; \quad \bar{\Lambda}_{12} = \Lambda_{12} + \bar{\lambda}_{12}; \quad \Lambda_{12} = 2\bar{\lambda}_{12}^2(1 - \lambda_{12} - \bar{\lambda}_{12})^{-1}, \quad (6)$$

where $\lambda_i \sim W_{ii,ii}$ are the intraband coupling constants ($i = 1, 2$); $\lambda_{12} \sim W_{12,12}$ is the constant of the direct interband interaction; the constants $\bar{\lambda}_{12} \sim W_{12,11} = W_{11,12}$ and $\bar{\lambda}_{12} \sim W_{12,21} = W_{11,22}$ describe the one-particle and two-particle virtual interband transitions; $L = \ln(\bar{\omega}_{ph}/T_c)$ is the Cooper logarithm; and $\bar{\omega}_{ph}$ is the average frequency of the phonon spectrum. From (5) we find¹⁸

$$T_c = \bar{\omega}_{ph} e^{-1/\bar{\Lambda}}; \quad \bar{\Lambda} = \max \left\{ \frac{2(\Lambda_1 \Lambda_2 - \bar{\Lambda}_{12}^2)}{\Lambda_1 + \Lambda_2 \pm \sqrt{(\lambda_1 - \lambda_2)^2 + 4\bar{\Lambda}_{12}^2}} \right\}. \quad (7)$$

In particular, with $\lambda_1 \approx \lambda_2 \approx \lambda > 0$ and $\Lambda_{12} > 0$, the effective coupling constant is given by the following expression, according to (6) and (7):

$$\bar{\Lambda} \approx \lambda + \bar{\lambda}_{12} + 4\bar{\lambda}_{12}^2(1 - \lambda_{12} - \bar{\lambda}_{12})^{-1}. \quad (8)$$

This effective coupling constant may be much larger than that in a one-band superconductor, $\lambda = N(0)W$, where $N(0)$ is the one-particle density of states at the Fermi level. It is probably for this reason that a superconductivity with fairly high transition temperatures $T_c > 20$ K arises in A_3C_{60} , as the result of a splitting of the conduction band (due to deformation vibrations of C_{60} molecules) and virtual interband transitions.⁴⁾ With $x \neq 3$, the disorder introduced by the dopant mixes band states differing in symmetry and thereby reduces the effectiveness of the Jahn–Teller mechanism for superconductivity. This circumstance might explain the sharp peak in T_c at the stoichiometric composition ($x = 3$) of the doped fullerites A_xC_{60} .

4. An increase in T_c would also be promoted by the multivalley nature of the band spectrum of the A_3C_{60} crystals, whose Brillouin zone contains, according to the calculations of Ref. 16, six deepest nondegenerate valleys at X points and eight equivalent degenerate valleys with a high density of states at L points. According to Ref. 17, when we take the multiply connected nature of the Fermi surface and the intervalley Cooper pairing into account in this case, we should replace the constant λ in (8) by the quantity

$$\bar{\lambda} = \lambda + (l - 1)[2\tilde{\kappa} + (l - 1)\bar{\kappa}], \quad (9)$$

where $l = 8$ or 6 , and $\tilde{\kappa}$ and $\bar{\kappa}$ are the constants of one-particle and two-particle intervalley transitions.⁵⁾ Crystals consisting of the huge fullerenes C_n with $n \geq 70$, on the other hand, are anisotropic, and the number of equivalent valleys in their Brillouin zones should be smaller than that in the Brillouin zone of the isotropic cubic crystal A_3C_{60} .

Furthermore, because of the lower initial symmetry of the C_n molecules with $n \geq 70$, the actual electron terms have no degeneracy, so there is no Jahn–Teller effect. It is accordingly extremely likely that when A_xC_{70} is doped, the Fermi level intersects only one nondegenerate band (or valley). The transition temperature T_c would then be given by the usual BCS expression $T_c = \bar{\omega}_{ph} e^{-1/\lambda}$. It thus follows that, under the conditions $\lambda \ll \bar{\Lambda}$, $\bar{\lambda}$ [see (8) and (9)], systems containing the hyperfullerene C_{70} should either exhibit T_c 's far lower than those in the C_{60} -based systems or have no superconductivity at all. These conclusions agree with the experimental data which we mentioned above.¹¹

We note in conclusion that a pseudo-Jahn–Teller effect in symmetric oxygen octahedra might also promote an increase in T_c in the cubic $BaBiO_3$ crystal, with the perovskite structure, when doped with K atoms.⁶ In the layered cuprate metal oxides, with a disrupted perovskite symmetry, on the other hand, the nature of the high- T_c superconductivity might be different (Ref. 25, for example). However, this difference would not diminish the important role played by the electron–phonon coupling as the basis of the high- T_c superconductivity.

- ¹⁾This comment also applies to other proposed mechanisms for the superconductivity of fullerites which are based on an electron-phonon coupling with acoustic phonons¹² or with optical vibrations,^{13,14} in which the "individuality" of the fullerene C₆₀, which would promote a superconductivity, is not reflected.
- ²⁾All interstitial sites in the A₃C₆₀ system are occupied, so the symmetry of the lattice and the Brillouin zone is not disrupted.
- ³⁾It may be that a coherent interband Cooper pairing cannot occur if a dynamic mechanism is operating to lift the band degeneracy. This case would stand in contrast with the standard model of a multiband superconductor^{19,20} with a multiply connected Fermi surface.
- ⁴⁾If the constants $\tilde{\lambda}_{12} \sim \tilde{\lambda}_{13} \sim \chi_{\nu\nu}$ (with $\nu \neq \nu'$) are much greater than λ , the frequency of the "soft" Jahn-Teller mode (ω_0) should be substituted into the coefficient of the exponential function in (7). This frequency may be much lower than $\bar{\omega}_{ph}$. In this case there may be a pronounced anharmonicity of the intramolecular vibration, manifested in (for example) anomalies in the isotope effect.^{21,22}
- ⁵⁾If we ignore the intervalley pairing of electrons, we find $\tilde{\lambda}' = \lambda + (l-1)\kappa$ instead of (9) (Ref. 23). For $x \neq 3$, the elastic scattering of electrons by disordered impurity atoms mixes states from different valleys, and the strengthening of the electron-phonon coupling as the result of virtual intervalley transitions is suppressed (the situation is analogous to that in a dirty superconductor²⁴).

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