Strong Superconductivity with Local Jahn-Teller Phonons in C_{60} Solids

J. E. Han,[1] O. Gunnarsson,[2] and V. H. Crespi[1]

[1]*Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802-6300, USA*
[2]*Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany*

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We analyze fulleride superconductivity at experimental doping levels, treating the electron-electron and electron-phonon interactions on an equal footing, and demonstrate that the Jahn-Teller phonons create a local (intramolecular) pairing which is surprisingly resistant to the Coulomb repulsion, despite the weakness of retardation in these low-bandwidth systems. The requirement for coherence throughout the solid then yields a very strong doping dependence to T_c, one consistent with experiment and much stronger than expected from standard Eliashberg theory.

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The superconductivity in alkali-doped A_xC_{60}, persisting up to very high temperatures ($T_c = 33$ K [1] or $T_c = 40$ K [2]), raises important questions about superconductivity in low-bandwidth molecular solids. Superconductivity arises from an effective attractive interaction between electrons. In conventional superconductors, it is argued that the effects of the strong Coulomb repulsion U are drastically reduced by retardation [3]. The weak phonon-induced attraction can then win and cause superconductivity. In the theory of conventional superconductors, the large U is therefore replaced by a weak empirical Coulomb pseudopotential μ^*. Retardation is, however, small for the fullerides [4], since the molecular vibration frequencies $\omega_{\rm ph}$ are comparable to the bare electron bandwidth W. U is therefore not expected to be drastically reduced by retardation for A_xC_{60}.

It is therefore important to treat the electron-electron and electron-phonon interactions on an equal footing, rather than replacing U by an empirical μ^*. We find that the interplay between these interactions leads to a local pairing of the electrons for molecular systems with Jahn-Teller phonons. This new mechanism is important for superconductivity and it is actually helped by the Coulomb repulsion. Superconductivity is therefore not greatly counteracted by the Coulomb repulsion in A_xC_{60}, in spite of the lack of important retardation effects. We demonstrate the crucial difference between Jahn-Teller and non–Jahn-Teller phonons. The general form of our model suggests that other Jahn-Teller systems, including high-temperature superconductors, should be examined carefully for a direct or indirect role of the phonons on superconductivity.

Conventional superconductors are studied in the Migdal-Eliashberg theory, assuming that $W \gg \omega_{\rm ph}$. For fullerides with $\omega_{\rm ph} \sim W$, the Eliashberg theory is of questionable accuracy. The failure of the Eliashberg theory is typically thought to lower T_c [5] (although the opposite has also been argued [6]). However, we find that T_c for fullerides is *not* generally lower than expected from Eliashberg theory. In the strongly correlated regime, the conventional Eliashberg separation of the electron-phonon and Coulomb interactions [7] becomes questionable. We show that this separability breaks down, as revealed by a very strong doping dependence of T_c, a dependence which is consistent with experimental observations [8].

In alkali-doped C_{60}, the threefold degenerate t_{1u} level is partly occupied and couples strongly to eight H_g intramolecular Jahn-Teller phonons. We capture the essential physics using a model with one t_{1u} level and one H_g mode per molecule. We also include the hopping between the molecules and the Coulomb repulsion between two electrons on the same molecule [9].

$$H = -\sum_{ijm\sigma} t_{ij} c^\dagger_{im\sigma} c_{jm\sigma} + U \sum_{imm'} n_{im\uparrow} n_{im'\downarrow} + \omega_{\rm ph} \sum_{i\nu} b^\dagger_{i\nu} b_{i\nu} + g \sum_{imm'\sigma\nu} V^{(\nu)}_{mm'} c^\dagger_{im\sigma} c_{im'\sigma} (b_{i\nu} + b^\dagger_{i\nu}). \quad (1)$$

$c^\dagger_{im\sigma}$ ($c_{im\sigma}$) is the electron creation (annihilation) operator acting on-site i, orbital m ($= 1, \ldots, 3$) and spin σ. $b^\dagger_{i\nu}$ ($b_{i\nu}$) is the phonon creation (annihilation) operator with the vibration mode ν ($= 1, \ldots, 5$). t_{ij} is the hopping integral, U the on-site Coulomb interaction, $\omega_{\rm ph}$ the phonon frequency, and g the electron-phonon coupling constant. We use a featureless semielliptical density of states. The coupling matrices $V^{(\nu)}$ are determined by icosahedral symmetry [10]. The dimensionless electron-phonon coupling constant λ is $\frac{5}{3} g^2 N(0)/\omega_{\rm ph}$, with $N(0)$ the density of states at Fermi energy. Typical parameters are $\lambda \sim 0.5$–1, $\omega_{\rm ph}/W \sim 0.1$–$0.25$, and $U/W \sim 1.5$–2.5 [11]. The model explicitly includes Jahn-Teller coupling with no restrictions on the ratio $\omega_{\rm ph}/W$ or the value of λ. We refer to this model as the $t \times H$ problem.

We can treat the electron-electron and electron-phonon interactions on the same footing and avoid the limitations of Eliashberg theory by using the dynamical mean-field theory (DMFT) [12]. The electron self-energy is assumed to be momentum independent, allowing a mapping of the lattice problem onto an effective impurity problem. The

DMFT is an exact theory in infinite dimension and is expected to be a good approximation for an fcc C solid with a large coordination number (12) and strong local interactions. We solve the effective impurity model using the discrete Hubbard-Stratonivich decoupling scheme [13,14] for the Coulomb interaction terms by introducing auxiliary boson fields. Monte-Carlo sampling is then performed, treating the phonon displacement fields $Q_{i\nu}[\equiv (b_{i\nu}^\dagger + b_{i\nu})/\sqrt{2}]$ and the auxiliary boson fields on equal footing [5,9]. This fully quantum mechanical treatment of phonons does not make any assumptions on adiabaticity.

We study superconductivity by applying a perturbation creating electron pairs and calculating the corresponding response function, i.e., the uniform ($\mathbf{q} = 0$) pairing susceptibility χ. A divergence of χ below a temperature T_c signals the onset of superconductivity. More details can be found in Ref. [15]. We start from the Bethe-Salpeter equation,

$$\chi = (\chi_0^{-1} - \Gamma)^{-1} = (1 - \chi_0\Gamma)^{-1}\chi_0, \tag{2}$$

where $\chi_0(\tau_1, \tau_2) = \sum_{\mathbf{k}} G(\mathbf{k}, \tau_1 - \tau_2)G(-\mathbf{k}, \tau_2 - \tau_1)$, which describes two independently propagating electrons (or holes) at zero net momentum.

To obtain χ and the effective interaction Γ within DMFT, we compute a

$$\chi^{\mathrm{loc}}(\tau_1,\tau_2, \tau_3, \tau_4) = -\sum_{mm'} \langle T[c_{m\uparrow}^\dagger(\tau_1)c_{m\downarrow}^\dagger(\tau_2)c_{m'\downarrow}(\tau_3)c_{m'\uparrow}(\tau_4)]\rangle, \tag{3}$$

where $\langle \cdots \rangle$ denotes a thermal average and m labels the t_{1u} levels on one molecule. As in Eq. (2), we construct the Bethe-Salpeter equation for local quantities,

$$\chi^{\mathrm{loc}} = [(\chi_0^{\mathrm{loc}})^{-1} - \Gamma^{\mathrm{loc}}]^{-1}. \tag{4}$$

$\chi_0^{\mathrm{loc}}(\tau_1, \tau_2) = G^{\mathrm{loc}}(\tau_1 - \tau_2)G^{\mathrm{loc}}(\tau_2 - \tau_1)$ with a local electron Green function $G^{\mathrm{loc}}(\tau_1 - \tau_2) = \sum_{\mathbf{k}} G(\mathbf{k}, \tau_1 - \tau_2)$. We assume $\Gamma \approx \Gamma^{\mathrm{loc}}$, which should be a good approximation, since the interaction is dominated by intramolecular phonons and an intramolecular Coulomb repulsion. Since χ_0 and χ_0^{loc} can be calculated within DMFT, χ follows from Eqs. (2)–(4).

The superconducting instability is determined by two factors, χ_0 and Γ, as in Eq. (2). For superconductivity, the effective interaction must be attractive ($\Gamma > 0$) and the system must have nonzero metallic weight to bring the local pairing fluctuations into coherence. For a metallic state, χ_0 diverges as $\chi_0(i\omega_n) \approx zN(0)/\pi|\omega_n|$ for Matsubara frequency $\omega_n \to 0$, where z is the quasiparticle renormalization factor near the chemical potential. Such a metallic state together with $\Gamma > 0$ leads to a singularity in χ as T is reduced.

The Jahn-Teller character of the phonons favors a local pairing of the electrons, which is very helpful for superconductivity. To better understand the fundamental mechanism, we first consider the local limit of the simplest Jahn-Teller problem; a doublet electronic state (e) coupling to a doublet Jahn-Teller phonon (E), i.e., $e \times E$ problem. The dynamical Jahn-Teller effect favors the formation of a local singlet [10,16–19]

$$\frac{1}{\sqrt{2}} \sum_m c_{m\uparrow}^\dagger c_{m\downarrow}^\dagger |0\rangle, \tag{5}$$

where the spin-up and spin -down electrons have the same m quantum number, i.e., a local pairing. Since χ^{loc} describes the removal (or addition) of a pair of electrons with the same m quantum number, the local pairing enhances χ^{loc}. For noninteracting electrons, on the other hand, hopping tends to distribute the electrons randomly over the molecular levels. This makes it more difficult to add or remove an electron pair with the same m quantum numbers. As a result, χ_0^{loc} tends to be smaller than χ^{loc}. Equation (4) shows that this implies an attractive Γ^{loc}. Thus, the local pairing favors an attractive Γ^{loc}.

For small U, the local pairing becomes less efficient, because charge fluctuations induced by electron hopping disrupt the Jahn-Teller ground state(s) into uncorrelated electron pairs. As U is increased, however, electron hopping is suppressed and the local pair formation becomes more important. The Coulomb interaction actually helps local pairing. This is one of the main results of this paper.

To illustrate this, we derive a sum rule. Putting $\tau_1 = \tau_2$, $\tau_3 = \tau_4$ and taking the Fourier transform with respect to $\tau_1 - \tau_3$ in the $T \to 0$ limit, we obtain

$$\chi^{\mathrm{loc}}(i\omega_n) = \int_0^\infty \rho^{\mathrm{loc}}(\varepsilon)/(\varepsilon - i\omega_n), \tag{6}$$

where

$$\rho^{\mathrm{loc}}(\varepsilon) = \sum_n \left| \langle n, N-2 | \sum_m c_{m\uparrow}c_{m\downarrow} | 0, N\rangle \right|^2 \times \delta[\varepsilon - E_0(N) + E_n(N-2)] + \cdots. \tag{7}$$

Here, $|n, N\rangle$ is the nth excited state of the system with N electrons and the energy $E_n(N)$. The term shown describes the removal of an electron pair; "$\cdots$" indicates the addition of an electron pair. In the limiting case of a large λ and a large U, we find a simple sum rule,

$$\int_0^\infty \rho^{\mathrm{loc}}(\varepsilon)\, d\varepsilon \equiv P = 2. \tag{8}$$

In contrast, for $\rho_0^{\mathrm{loc}}(\varepsilon)$, the corresponding sum rule gives only $P_0 = 1$, since χ_0 in Eq. (2) represents independently propagating electrons (holes), without any preference for the electrons having the same m quantum number.

In Fig. 1, exact diagonalization results for an impurity model in finite clusters demonstrate the effective local pairing of Jahn-Teller systems. The $e \times E$ system shows enhanced static pairing susceptibility χ and sum-rule P

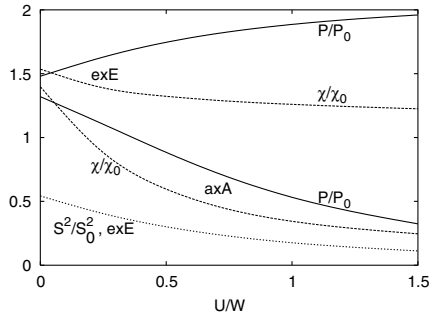

FIG. 1. The ratios P/P_0, $\chi^{\rm loc}/\chi_0^{\rm loc}$, and $\langle S^2\rangle/\langle S^2\rangle_0$ as a function of U/W. Exact diagonalization was performed for an impurity model with five host sites using $\lambda = 0.6$. For the non–Jahn-Teller model $a \times A$, the ratios P/P_0 and $\chi^{\rm loc}/\chi_0^{\rm loc}$ drop rapidly as U increases. In contrast, the pairing susceptibility for $e \times E$ is very resistant to increasing U. This is due to the local pairing (singlet formation), as shown by $\langle S^2\rangle/\langle S^2\rangle_0$.

over the unpaired limit ($\chi^{\rm loc}/\chi_0^{\rm loc}$, $P/P_0 > 1$) at all U. To further illustrate the local singlet formation, we calculate $\langle S^2\rangle$, where S is the spin operator of the impurity. This is divided by the corresponding result $\langle S^2\rangle_0$ for noninteracting electrons. $\langle S^2\rangle/\langle S^2\rangle_0$ drops rapidly as U is increased, due to the local singlet formation, while for $\lambda = 0$ it would have increased from 1 to 4/3. As a comparison, the figure also shows results for a system with a nondegenerate electronic state (a) coupled to a nondegenerate non–Jahn-Teller phonon (A), i.e., an $a \times A$ problem. In this case, pairing goes away as U is increased, as suggested by $\chi^{\rm loc}/\chi_0^{\rm loc}$, $P/P_0 < 1$. The effective interaction $\Gamma^{\rm loc}$ therefore rapidly becomes repulsive for the $a \times A$ case, while it stays attractive for the $e \times E$ case. For the $a \times A$ case, $\langle S^2\rangle/\langle S^2\rangle_0$ (not shown in the figure) increases from 0.67 to 1.68 as U/W is increased from 0. to 1.5. Capone *et al.* [20] have reached somewhat similar conclusions using a different approach.

We now turn to the DMFT with explicit results for superconducting transitions, beginning with $U = 0$. Figure 2 shows T_c as a function of λ according to DMFT and Eliashberg theories [21]. The $t \times H$ and $a \times A$ cases give rather similar values of T_c for small and intermediate values of λ. For larger values of λ, T_c has a maximum and then drops. This drop is due to a rapid reduction of χ_0 due to strong mass renormalization. This happens already for $\lambda \gtrsim 0.6$ for the $a \times A$ model from strong charge fluctuations [5] caused by coupling to A_g phonons, but for a larger value of λ for the $t \times H$ model. The Eliashberg theory is expected to overestimate T_c of doped C_{60} because of the violation [5] of Migdal's theorem. We find that this does not happen until the system gets close to the metal-insulator instability. For small λ, χ_0 goes as $1/(1 + \lambda)$, which renormalizes λ to $\lambda/(1 + \lambda)$ in the McMillan equation [7], and is properly described in the Eliashberg theory. For a larger λ, however, χ_0 drops much faster in the DMFT than in the perturbative McMillan or Eliashberg theories, where the electron

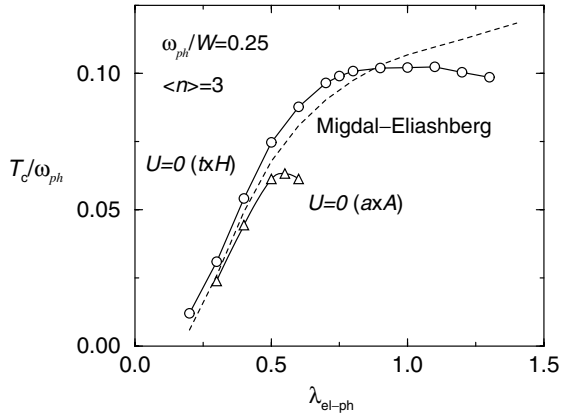

FIG. 2. T_c as a function of λ according to Migdal-Eliashberg (dashed line) and DMFT theories for the $t \times H$ (○) and $a \times A$ (△) couplings at half filling. The parameters are $\omega_{\rm ph}/W = 0.25$ and $U = 0$.

self-energy is considered only up to the leading order. The strong mass renormalization results in spectral weight transfer from the chemical potential and weak coherence of electron pairs, thereby reducing T_c.

Figure 3 shows T_c as a function of U for the $t \times H$ and $a \times A$ models. For $a \times A$, the phonon-induced attractive interaction $U_{\rm ph}$ is of the order of $U_{\rm ph}/W \sim -0.47$. We therefore expect T_c to vanish when $U + U_{\rm ph} \gtrsim 0$, as is indeed found. For the Jahn-Teller system $t \times H$, the attractive interaction is smaller, $U_{\rm ph}/W \sim -0.2$. This attractive interaction is therefore quickly overwhelmed by the Coulomb repulsion. Superconductivity remains, however, even for $U + U_{\rm ph} \gg 0$, and T_c drops surprisingly slowly as U is increased. The reason is that local pairing arises from correlation of spin and orbital structures within each site, and therefore is not suppressed by the charge interaction [22,23]. Superconductivity is expected to exist in the metal right up to the Mott transition. Figures 2 and 3 demonstrate an unexpected failure mode

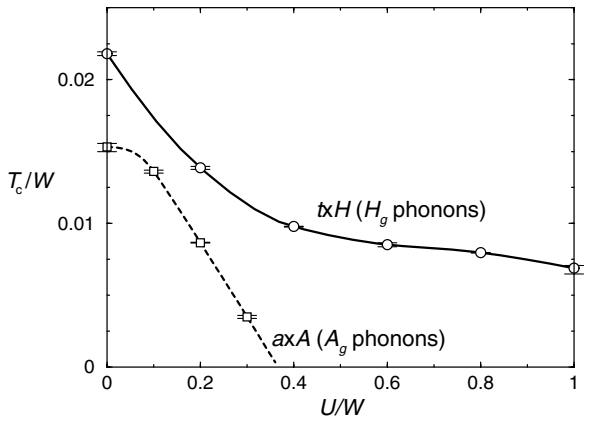

FIG. 3. T_c as a function of U for the $t \times H$ and $a \times A$ models for half filling. The parameters are $\lambda = 0.6$ and $\omega_{\rm ph}/W = 0.25$. The figure illustrates the important difference between H_g and A_g phonons.

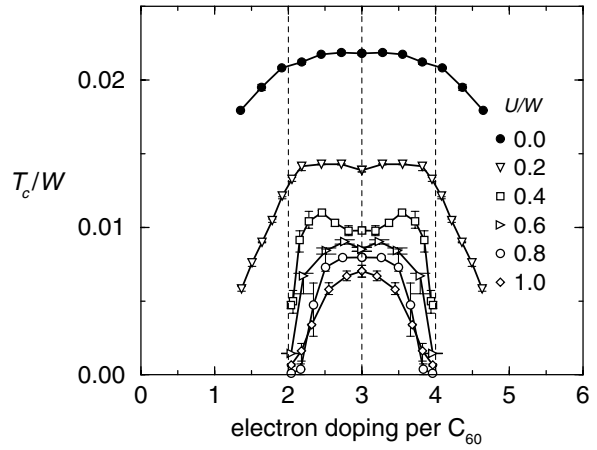

FIG. 4. T_c as a function of doping n for different values of U for $t \times H$ coupling. The parameters are $\omega_{\rm ph}/W = 0.25$ and $\lambda = 0.6$. The figure illustrates the strong doping dependence for $U/W \geq 0.4$.

for Eliashberg theory: The problem is not that $\omega_{\rm ph} \sim W$, but the treatment of the Coulomb repulsion. Because of the local pairing, the Coulomb interaction enters very differently for Jahn-Teller and non–Jahn-Teller models, and it cannot be easily described by a Coulomb pseudopotential.

Experimentally, T_c drops quickly in fullerides when the doping n is reduced below three electrons per C_{60} molecule [8]. This cannot be explained within Eliashberg theory: Doping n away from 3 induces only a slight change of the density of states at the Fermi energy [24], which should not affect T_c greatly up to $n = 2, 4$. This has been taken as evidence for an electron-electron mechanism of superconductivity [25]. Figure 4 shows the doping dependence of T_c in DMFT. For small U, T_c drops slowly until $n \sim 2$ or 4 and then starts dropping much faster: $\Gamma^{\rm loc}$ drops rapidly here, because local pairing is inefficient once the average number of electrons per molecule drops below two. For $U/W > 0.4$, T_c drops very quickly as $n = 2, 4$ is approached. This is because of the strong tendency of a metal-insulator transition at even-number fillings; the system can gain a particularly large binding energy from Jahn-Teller coupling at even-number fillings ($n = 2, 4$) [16], which tends to localize electrons [9]. Despite the presence of an attractive interaction from the local pairing near $n = 2, 4$, weak coherence from the reduced metallic weight lowers T_c. The strong doping dependence can be explained within an electron-phonon mechanism, and there is no need to assume an electronic mechanism.

In fullerides, local pairing is crucial in reducing the effects of the Coulomb repulsion and overcoming the lack of retardation effects. This leads to new physics in the strongly correlated low-bandwidth solids, due to the interplay between the Coulomb and electron-phonon interactions. We furthermore find that the Eliashberg theory breaks down in these systems because of the closeness to a metal-insulator transition, not because $\omega_{\rm ph} \sim W$. This framework can naturally explain the strong doping dependence of T_c in $A_n C_{60}$. The importance of local pairing is consistent with the short coherence length, which is only about 3 times the C_{60}-C_{60} separation [26,27].

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