Nonadiabatic Channels in the Superconducting Pairing of Fullerides

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We show the intrinsic inconsistency of the conventional phonon mediated theory of superconductivity in relation to the observed properties of Rb_3C_{60}. The recent, highly accurate measurement of the carbon isotope coefficient $\alpha_C = 0.21$, together with the high value of T_c (30 K) and the very small Fermi energy E_F (0.25 eV), unavoidably implies the opening of nonadiabatic channels in the superconducting pairing. We estimate these effects and show that they are actually the key elements for the high value of T_c in these materials compared to the very low values of graphite intercalation compounds.

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One of the most striking evidences of the phonon role in high-temperature superconductivity of alkali-doped C_{60} compounds is the observation of the nonzero isotope effect on the value of the critical temperature T_c [1]. However, the large spread of the reported values of the carbon isotope coefficient $\alpha_C = -d\ln T_c/d\ln M$ [2], where M is the isotopic mass, has prevented us from settling upon a definitive and self-consistent picture. This long-standing uncertainty has been solved only recently for the compound Rb_3C_{60} ($T_c \simeq 30$ K). Resistive measurements on 99% enriched ^{13}C single crystals have permitted us, in fact, to establish $\alpha_C = 0.21$ with high precision [3].

Knowledge of the accurate value of α_C is an important element to establish not only the important role of phonons but also to test the self-consistency of the Migdal-Eliashberg (ME) theory of superconductivity [4,5] in alkali-doped fullerenes. The measured values $\alpha_C = 0.21$ and $T_c = 30$ K can be used to extract the microscopic quantities involved in the superconducting pairing. For example, in Ref. [3], $T_c = 30$ K and $\alpha_C = 0.21$ are interpreted within the conventional ME theory by $\lambda = 0.9$, $\omega_{\ln} = 1360$ K, and $\mu^* = 0.22$, where λ is the electron-phonon coupling constant, $\omega_{\ln}$ is the logarithmic phonon frequency, and μ^* is the Coulomb pseudopotential [6]. According to this standard analysis, the high value of T_c in alkali-doped C_{60} compounds is merely due to a strong electron-phonon coupling to the highest intramolecular phonon modes. These results should be compared with the graphite intercalation compounds (GIC) where $T_c \simeq 0.2$ K [7] is explained by a moderate coupling ($\lambda \simeq 0.3$) to similar high energy phonon modes. Current theories claim that the big difference between the electron-phonon coupling in fullerides compared with graphite intercalation compounds arises from the finite curvature of the C_{60} molecule [8]. In this perspective, therefore, Rb_3C_{60} is just an ordinary strong-coupling superconductor described by the conventional adiabatic ME framework.

In this Letter instead we demonstrate the intrinsic inconsistency of the standard ME theory in Rb_3C_{60}. This conventional description is, in fact, invalidated by the extremely low value of the Fermi energy $E_F \simeq 0.25$ eV $\simeq$ 2900 K characteristic of the fullerene compounds [1]. We show that the whole range of λ-ω_{ph} values which fit $T_c = 30$ K and $\alpha_C = 0.21$ through the solution of the standard ME equations implies a Migdal parameter $\lambda\omega_{ph}/E_F$ larger than 0.4, instead of being zero as assumed by the ME theory [4,5]. This situation inevitably leads to the breakdown of Migdal's theorem and to the opening of nonadiabatic channels in the superconducting pairing [9]. By solving the nonadiabatic equations [10,11], we estimate these effects and show that they are actually the key elements for the high values of T_c in the fullerene compounds.

We now discuss why the experimental data $T_c = 30$ K and $\alpha_C = 0.21$ [3] are inconsistent with respect to the ME theory. To simulate the coupling of the electrons to the different intramolecular phonon modes, we consider an electron-phonon spectral function $\alpha^2F(\omega)$ modeled as a rectangle of width $\Delta\omega_0$ and centered at ω_0. For $\Delta\omega_0 = 0$, $\alpha^2F(\omega)$ reduces to a single Einstein δ peak while for $\Delta\omega_0 > 0$ it becomes broadened. The electron-phonon coupling constant is determined by the usual relation $\lambda = 2\int d\omega\, \alpha^2F(\omega)/\omega$. The Coulomb pseudopotential is taken to have the standard form $\mu^* = \mu/[1 + \mu\ln(\omega_c/\omega_{\max})]$, where $\omega_{\max} = \omega_0 + \Delta\omega_0/2$ is the maximum phonon frequency, μ is the screened Coulomb parameter, and ω_c is the high-frequency cutoff. According to whether it is the entire set of π bands [12] or rather only the narrow conducting t_{1u} band [13] which contributes to the dynamical screening, we shall consider $\omega_c = 5\omega_{\max}$ or $\omega_c = E_F =$ 2900 K, respectively. For different values of $\Delta\omega_0/\omega_0$ we then solve numerically the ME equations to find the values of λ, ω_0, and μ (or μ^*) which reproduce the experimental data $T_c = 30$ K and $\alpha_C = 0.21$.

In Fig. 1 we show the calculated μ and μ^* (upper panel) and ω_0 (lower panel) as a function of λ for $\Delta\omega_0/\omega_0 = 0$ (solid lines) and for $\Delta\omega_0/\omega_0 = 1$ (dashed lines) with $\omega_c = 5\omega_{\max}$. The main point of Fig. 1 is that the calculated ω_0 depends strongly on the electron-phonon constant λ. For large values of λ, $T_c = 30$ K and $\alpha_C = 0.21$

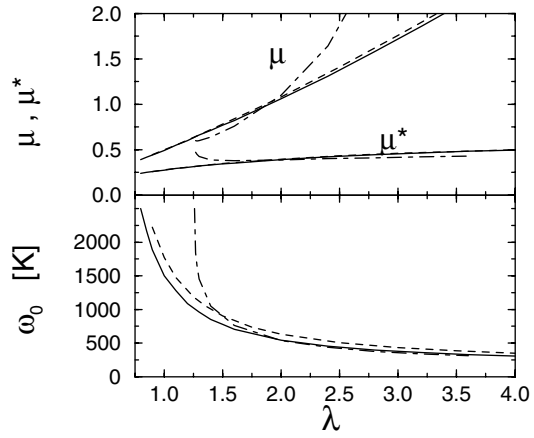

FIG. 1. Plot of the Coulomb parameters μ and μ^* (upper panel) and of the central phonon frequency ω_0 (lower panel) obtained by the standard ME equations constrained to have $T_c = 30$ K and $\alpha_C = 0.21$. Solid lines: $\Delta\omega_0/\omega_0 = 0$, $\omega_c = 5\omega_{max}$; dashed lines: $\Delta\omega_0/\omega_0 = 1$, $\omega_c = 5\omega_{max}$; dash-dotted lines: $\Delta\omega_0/\omega_0 = 0$, $\omega_c = E_F$.

are reproduced only for quite small phonon frequencies while decreasing λ quickly enhances ω_0. The C_{60} phonon spectrum, however, is limited by a maximum frequency of $\sim$2300 K [1,14], and this settles a lower limit for the allowed values of λ. In fact, from the lower panel of Fig. 1, it is clear that for λ smaller than 1 the corresponding $\omega_{max} = \omega_0 + \Delta\omega_0/2$ rapidly exceeds 2300 K signaling that the solution of the ME equations falls well outside the range of applicability for the fullerene compounds.

A further interesting point is that the effect of the spectral broadening ($\Delta\omega_0 > 0$) is of secondary importance to the overall behavior, suggesting that the results are only weakly affected by the detailed structure of $\alpha^2F(\omega)$. In fact, for $\lambda = 0.9$ we find $\mu^* \simeq 0.25$, $\omega_{ln} \simeq 1873$ K ($\Delta\omega_0 = 0$), and $\omega_{ln} \simeq 1555$ K ($\Delta\omega_0 = \omega_0$), where $\omega_{ln} = \exp[(2/\lambda)\int d\omega \ln\omega\alpha^2F(\omega)/\omega]$ is the logarithmic phonon frequency which, for the rectangular model here considered, is given by $\omega_{ln} = [\omega_0^2 - (\Delta\omega_0/2)^2]^{1/2}$. These values are consistent with those reported in Ref. [3] ($\lambda \simeq 0.9$, $\mu^* \simeq 0.22$, $\omega_{ln} \simeq 1360$ K) where a phonon spectrum obtained by *ab initio* calculations has been used to fit $T_c = 30$ K and $\alpha_C = 0.21$.

In Fig. 1 we show also the results for $\Delta\omega_0 = 0$ and $\omega_c = E_F$ (dash-dotted lines). Because of the reduced dynamical screening of the Coulomb repulsion, the increase of ω_0 is much steeper than the previous cases until at $\lambda \simeq 1.25$ we find $\omega_0 \simeq E_F$ and $\mu^* \simeq \mu$ so that it is no longer possible to have α_C smaller than the BCS value 0.5.

We now address the consistency of the data of Fig. 1 with the standard ME theory [4,5]. The assumption at the basis of the ME framework is Migdal's theorem which states that, as long as the phonons have a much slower dynamics than that of the electrons, the nonadiabatic electron-phonon interference effects (vertex processes) can be neglected [4]. This condition is well satisfied in conventional superconductors since their Fermi energy is of order $E_F \sim 10$ eV $\sim 10^5$ K, while the highest phonon frequencies are usually less than $\sim$50 meV $\sim$ 60 K [6]. However, the alkali-doped fullerene compounds are molecular solids characterized by very narrow conduction electron bands of width of only $W \simeq 0.5$ eV [1]. In Rb_3C_{60} (as in the other A_3C_{60} compounds) the conduction band is half filled by electrons and the corresponding Fermi energy is $E_F \simeq 0.25$ eV $= 2900$ K, while the maximum phonon frequency is $\sim$2300 K. In principle, therefore, there is no reason to expect Migdal's theorem to be applicable in fullerene compounds, unless the main interaction is with the lowest C_{60} phonon modes ($\sim$400 K) via, however, a rather weak coupling.

We can test whether the data of Fig. 1 are consistent with Migdal's theorem by evaluating the order of magnitude (P) of the first nonadiabatic electron-phonon vertex correction. By following the same reasonings as Migdal [4,10], this is given by

$$P = 2\int_0^{+\infty} d\omega\, \frac{\alpha^2F(\omega)}{E_F} \equiv \lambda\, \frac{\omega_{ph}}{E_F}, \qquad (1)$$

where for the rectangular model we considered the average phonon frequency ω_{ph} reduces to

$$\omega_{ph} = \frac{2}{\lambda}\int_0^{+\infty} d\omega\, \alpha^2F(\omega) = \frac{\Delta\omega_0}{\ln\left(\dfrac{\omega_0 + \Delta\omega_0/2}{\omega_0 - \Delta\omega_0/2}\right)}. \qquad (2)$$

When $P \to 0$ the nonadiabatic interferences are negligible and the ME theory holds true; on the contrary, sizable values of P signal the breakdown of the standard theory. In Fig. 2 we show the values of ω_{ph}/E_F (upper panel) and

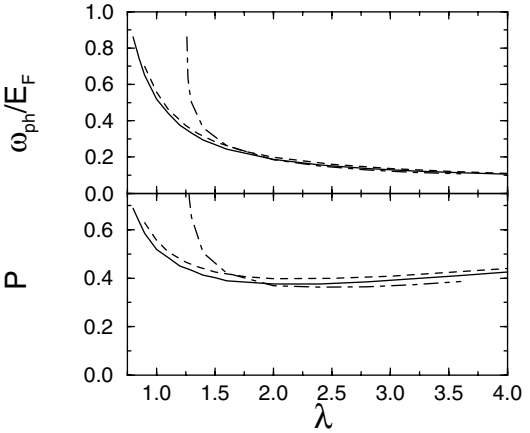

FIG. 2. Values of ω_{ph}/E_F (upper panel) and of $P = \lambda\omega_{ph}/E_F$ (lower panel) extracted from the data of Fig. 1 with $E_F = 0.25$ eV $= 2900$ K. Solid lines: Einstein phonon spectrum; dashed lines: broad spectrum with $\Delta\omega_0/\omega_0 = 1$; dash-dotted lines: Einstein phonon spectrum $\Delta\omega_0/\omega_0 = 1$ with $\omega_c = E_F$. The Migdal-Eliashberg theory holds true only when $\omega_{ph}/E_F \ll 1$ and $P \ll 1$.

of P (lower panel) extracted from the ω_0 values reported in Fig. 1 and by setting $E_F = 2900$ K. As expected from the overall trend of ω_0 vs λ plotted in Fig. 1, the adiabatic ratio ω_{ph}/E_F is large and close to unity for $\lambda < 1$, while it rapidly decreases to $\omega_{ph}/E_F \simeq 0.1$ for large values of λ. One could therefore argue that adiabaticity is guaranteed for very large electron-phonon couplings and that in this regime the ME framework is valid. This is, however, incorrect because according to (1) the vertex correction is proportional to λ so that, as shown in the lower panel of Fig. 2, *P is never negligible*. Note that the claimed value $\lambda \simeq 0.9$ [3] corresponds to $\omega_{ph}/E_F > 0.7$ and a minimum $P > 0.6$; i.e., the vertex correction is comparable to unity.

From Figs. 1 and 2 we conclude therefore that the conventional phonon-mediated superconductivity is not a complete and self-consistent picture of Rb_3C_{60} since the values of λ and ω_0 needed to fit $T_c = 30$ K and $\alpha_c = 0.21$ strongly violate Migdal's theorem. This conclusion holds true even when electron-phonon spectra more structured than the rectangular one are used to fit the data of Ref. [3]. By adding a δ peak centered at $\omega = \omega_1$ to a rectangular spectrum of width covering the whole intramolecular modes, we have, in fact, simulated additional contributions from low-frequency ($\omega_1 \simeq 50$ K) C_{60}-C_{60} phonon modes [15] and from an enhanced coupling to soft intramolecular modes [16] ($\omega_1 \simeq 400$–600 K) possibly related to dynamical Jahn-Teller effects [17]. We find that $T_c = 30$ K and $\alpha_C = 0.21$ imply $P > 0.4$ when $\omega_1 = 50$ K and $P > 0.45$ when $\omega_1 = 400$ K (further details will be presented elsewhere).

The above results point out that, if superconductivity in Rb_3C_{60} is mediated by phonons, a consistent description of its superconducting properties should be sought beyond the ME theory. More precisely, the low value of E_F indicates that the adiabatic hypothesis and Migdal's theorem should be abandoned from the start and that the theory should be formulated by allowing ω_{ph}/E_F to have values sensibly larger than zero. This naturally leads to nonadiabatic interference effects in the electron-phonon scattering which can significantly modify both the normal and superconducting properties with respect to the ME phenomenology [9].

Indeed, characteristic effects of the nonadiabatic vertex corrections are predicted to be observable in several quantities, such as T_c and its isotope coefficient [9,10], the reduction rate of T_c itself upon disorder [11], the effective electronic mass m^* [18], and the Pauli susceptibility [19]. A peculiar feature of the nonadiabatic processes is to produce, under some conditions, constructive electron-phonon interference in the particle-particle channel leading to an enhancement of T_c [9,10]. Hence $T_c = 30$ K, for a given phonon spectrum, can be achieved by much smaller values of λ than needed in conventional ME theory. Favorable conditions to this trend are expected in materials with strong electronic correlation, as fullerenes: strong local repulsion suppresses short-range interactions (large $\mathbf{q}$'s in Fourier space) and favors forward small-$\mathbf{q}$ scattering [20,21] for which electron-phonon vertex processes become attractive.

Now we reanalyze the experimental constraints of Rb_3C_{60}, $T_c = 30$ K and $\alpha_C = 0.21$, in the context of the nonadiabatic theory of superconductivity. We show that the inconsistencies of the results derived by ME theory are naturally solved when the same experimental data are coherently analyzed in the nonadiabatic regime.

Explicit analytical and diagrammatic equations of the nonadiabatic theory of superconductivity have been outlined in previous works [9–11] and, for the sake of shortness, they will be here omitted. A set of generalized Eliashberg equations in the nonadiabatic regime is constructed by following a perturbative approach based on the Migdal parameter P. The consistency of such a perturbative scheme is discussed below. We simplify the phonon spectrum by assuming a dispersionless Einstein phonon with energy ω_0. We note, however, that our results, as also shown in Figs. 1 and 2, are only weakly affected by the specific shape of $\alpha^2F(\omega)$. Electronic correlation is taken into account by a cutoff q_c on the electron-phonon exchanged momenta, which selects forward scattering, where the stronger the correlation the smaller the q_c.

In Fig. 3 we show the phonon frequency ω_0, the statically and dynamically screened Coulomb repulsion, respectively, μ and μ^*, vs λ obtained in the nonadiabatic theory to reproduce $T_c = 30$ K and $\alpha_C = 0.21$. The parameter q_c has been chosen $q_c = 0.2k_F$ (k_F is the Fermi vector), an appropriate value for a strongly correlated system, and the dynamical screening of μ has been considered to be provided by the t_{1u} electrons [13].

From the comparison of Fig. 3 with Fig. 1, the first remarkable difference lies in the distinct ranges of electron-phonon couplings needed to reproduce the Rb_3C_{60} data. In fact, the conventional ME theory predicts $\lambda \gtrsim 1$ (Fig. 1), while the nonadiabatic analysis yields $\lambda \lesssim 1$

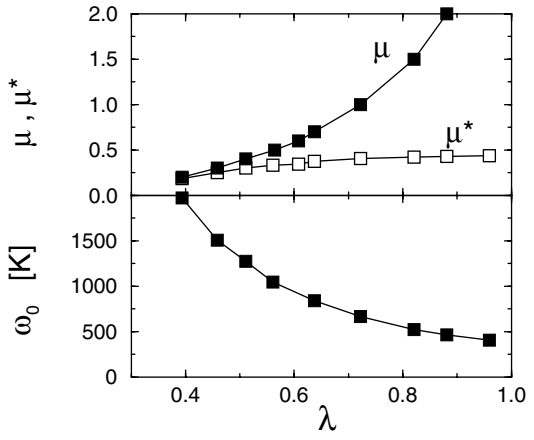

FIG. 3. Plot of μ, μ^*, and ω_0 calculated by the nonadiabatic theory as solutions of $T_c = 30$ K and $\alpha_C = 0.21$. Note that the range of values for λ is now much smaller and realistic with respect to those of Fig. 1.

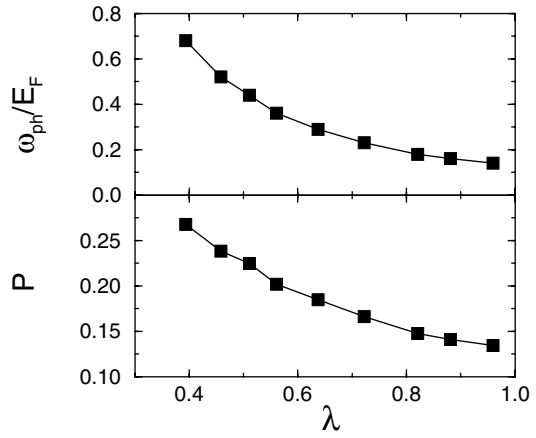

FIG. 4. Adiabatic ratio $\omega_{\rm ph}/E_{\rm F}$ and vertex correction magnitude P obtained by the nonadiabatic solutions of Fig. 3

(Fig. 3). But the most striking difference is that, if we now take the parameters obtained by the generalized theory and use them in the standard ME theory, these would give a very low value of T_c, less than 1 K or even zero. This result is now perfectly compatible with the GIC superconductors, for which Migdal's theorem holds true, and it clarifies that the high T_c values of the fullerides are essentially due to constructive nonadiabatic interference effects rather than to a very large value of λ. In our perspective, therefore, the origin of the enhancement from $T_c \simeq 0.2$ K in GIC to $T_c \simeq 20$–30 K in fullerene compounds stems mainly from the opening of the nonadiabatic channels in the electron-phonon interaction, rather than from a $\sim$300% enhancement of λ.

We address now the consistency of the perturbative scheme with the nonadiabatic solutions for Rb_3C_{60}. In Fig. 4 we show the adiabatic ratio $\omega_{\rm ph}/E_{\rm F}$ ($\omega_{\rm ph} = \omega_0$) and the Migdal's parameter P extracted from the data reported in Fig. 3. The large value of $\omega_{\rm ph}/E_{\rm F}$ shown in the upper panel points out again the breakdown of Migdal's theorem and consequently the need of the inclusion of the nonadiabatic vertex corrections. The magnitude of the vertex corrections $P \sim 0.2$, certainly not negligible, is, however, small enough to support a perturbative approach in P [9,10]. Note moreover that, according to the comparison with exact results for the single-electron Holstein model [22], for weak couplings the system is away from polaron formation and that the perturbative scheme is well defined.

In conclusion, we have investigated the validity of Migdal-Eliashberg theory of superconductivity in Rb_3C_{60} by analyzing the constraints imposed by recent experimental data, namely, the critical temperature $T_c = 30$ K and the isotope effect $\alpha_{\rm C} = 0.21$. We have found that the values of λ and $\omega_{\rm ph}$ needed to reproduce the experimental data, together with the very low value of the Fermi energy, strongly violate Migdal's theorem and are therefore inconsistent with the ME framework. This situation unavoidably leads to the opening of nonadiabatic channels in the electron-phonon pairing which we argue to play the primary role for the high values of T_c in fullerene compounds. Finally, we stress the importance of peculiar nonadiabatic effects in both superconducting [11] and normal state properties [18,19] of fullerene compounds. Experiments in this direction are, therefore, of great interest.

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