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Nonadiabatic Superconductivity in Fullerene-Based Materials¹

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Abstract—Fullerene compounds have phonon frequencies up to $\omega_{\max} = 0.2$ eV and a Fermi energy of the order $E_F = 0.3$ eV. It is, therefore, expected that the adiabatic parameter $\lambda\omega_{\text{ph}}/E_F$ (where λ is the electron–phonon coupling constant and ω_{ph} is a typical phonon frequency) is not *a priori* negligible and the conventional theory of phonon-mediated superconductivity is inapplicable in this case. Here, we discuss how the conventional theory is inconsistent with a number of experimental data and provide a generalization of the theory in order to include nonadiabatic electron–phonon effects. We show that the inclusion of nonadiabatic channels in the electron–phonon interaction is a key element for the high values of T_c in these materials. We make several predictions regarding the superconducting and normal-state properties of fullerene compounds that can be tested experimentally. © 2002 MAIK “Nauka/Interperiodica”.

It is certainly due to their apparently ordinary phenomenology that the superconductivity in C_{60} materials has often been assumed to be consistently described by the conventional Migdal–Eliashberg (ME) theory of phonon-mediated superconductivity [1, 2]. In favor of this point of view, we can enlist several features, such as the Fermi liquidlike normal-state properties, order parameter of *s*-wave symmetry, sizeable carbon isotope effect, etc. [3]. However, despite these reassuring properties, fullerene-based superconductors also display less ordinary features, making the ME picture problematic. In fact, like the high- T_c copper oxides, C_{60} compounds have extremely low charge carrier density [4], have a significant electron correlation, and are close to a metal–insulator transition, showing a strong dependence of T_c upon doping and disorder [3, 5]. Within the framework of the ordinary ME theory, all these features tend to degrade superconductivity.

The recent discovery of superconductivity at $T_c = 52$ K in hole-doped C_{60} [6] raises even more doubts as to the validity of the ME picture. In fact, $T_c = 52$ K is the highest critical temperature among non-cuprate superconductors (it also exceeds $T_c = 39$ K of the recently discovered MgB_2 superconductivity [7]) and it is difficult to understand why C_{60} should represent the best optimized ME material and, at the same time, display properties which degrade ME superconductivity.

In addition to the above conceptual difficulties, there are actually several hints opposing the ME scenario; this is disseminated in both experimental and theoretical published works on fullerenes. Let us consider, for example, what is known on the relevant energy scales involved in the electron–phonon interaction. The C_{60}

molecule has a rather wide range of phonon modes of energy extending from $\omega_{\min} = 400$ K to $\omega_{\max} = 2300$ K. The relevant bandwidth for both electron- and hole-doped materials is $W = 0.5$ eV = 5800 K; therefore, for the A_3C_{60} half-filled compounds, the Fermi energy is $E_F = 0.25$ eV = 2900 K [3]. The value of E_F for the optimum hole doping ($T_c = 52$ K) is even lower. Note that these are very small values compared to those of conventional superconductors, for which E_F is of several electronvolts. A great effort has been devoted in the past to the calculation of the electron–phonon interaction in C_{60} materials. In Fig. 1, we summarize several published results on A_3C_{60} compounds obtained using different calculation schemes [8]. In the figure, $V = \sum_i V_i$ is the total interaction arising from the coupling of the eight H_g C_{60} phonons to the t_{1u} electrons and $\omega_{\text{ph}} = \sum_i V_i\omega_i/V$, where ω_i is the frequency associated with the *i*th phonon mode. Figure 1 is quite illuminating since, although the discrepancies in the value of V among the different calculations are rather important, all these calculations agree in estimating the ratio ω_{ph}/E_F to be larger than 0.4. This result is in contradiction with the adiabatic hypothesis on which the entire ME framework rests. The ME equations of superconductivity are, in fact, defined only in the adiabatic limit $\omega_{\text{ph}}/E_F \rightarrow 0$, in which all the additional nonadiabatic vertex corrections can be neglected in virtue of Migdal’s theorem [1].

The analysis of the energy scales and the data of Fig. 1 represent the first evidence of the inadequacy of the ME theory of superconductivity in fullerenes. Another important indication stems from an analysis of the experimental data of Rb_3C_{60} ($T_c = 30$ K), for which

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a very accurate measurement of the carbon isotope coefficient $\alpha_C = -d\ln(T_c)/d\ln(M)$, where M is the isotopic carbon mass, became available only recently [9]. In fact, the measured value $\alpha_C = 0.21 \pm 0.012$ is sufficiently accurate to permit one to test the consistency of the ME theory by estimating the values of the electron-phonon coupling λ , of the phonon frequency ω_{ph} , and of the Coulomb pseudopotential μ^* that correspond to the experimental values of T_c and α_C for Rb_3C_{60} . To this end, we considered different models for the electron-phonon spectral function $\alpha^2F(\omega)$ and numerically solved the ME equations by inserting the values of λ , ω_{ph} , and μ^* that reproduce the experimental data $T_c = 30$ K and $\alpha_C = 0.21$. In Fig. 2, we show the results (filled squares) obtained by employing an Einstein phonon spectrum $\alpha^2F(\omega) = (\lambda\omega_{\text{ph}}/2)\delta(\omega - \omega_{\text{ph}})$. The main point of Fig. 2 is that the calculated ω_{ph} (lower panel) depends strongly on the electron-phonon coupling constant λ . Large values of λ , $T_c = 30$ K, and $\alpha_C = 0.21$ are reproduced only for quite small phonon frequencies, while decreasing λ quickly enhances ω_{ph} . The C_{60} phonon spectrum is, however, limited by a maximum phonon frequency of ~ 2300 K [3, 8], so that λ cannot be less than about 1.25. By using different shapes of the function $\alpha^2F(\omega)$ and of the frequency cutoff in μ^* , we can lower the minimum allowed value of λ to about $\lambda_{\text{min}} \approx 1.0$. Note that the obtained values of the Coulomb pseudopotential μ^* (Fig. 2, upper panel, filled squares) are always quite large compared to the standard value $\mu^* \approx 0.1$ [10].

According to the ME analysis, Rb_3C_{60} is, therefore, an intermediate- or strong-coupling superconductor. Let us now address the question of whether this conclusion is consistent or not with the ME framework [1, 2, 10]. As pointed out before, 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 interference effects (vertex corrections) can be neglected [1]. We can test whether the data of Fig. 2 are consistent with Migdal's theorem by making an order-of-magnitude estimate of the first nonadiabatic electron-phonon vertex correction P . According to Migdal [1], P is given by

$$P = \lambda \frac{\omega_{\text{ph}}}{E_F}. \quad (1)$$

Conventional superconductors, such as Pb and Al, have Fermi energies of the order of $E_F \sim 5$ to 10 eV, phonon frequencies usually not exceeding ~ 50 meV, and λ less than about 1–1.5 [10]. Hence, for conventional materials, $P \ll 1$, the vertex corrections are negligibly small and the ME framework is well founded. To estimate the value of P in Rb_3C_{60} , we insert the value of λ and ω_{ph} resulting from our solution of the ME equations into Eq. (1). We obtain that, for any couple of values of λ and ω_{ph} from Fig. 2 (lower panel, filled

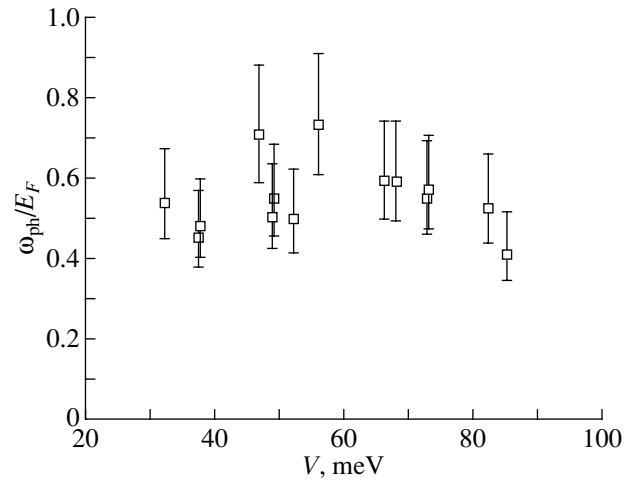


Fig. 1. Adiabatic parameter ω_{ph}/E_F versus electron-phonon pairing interaction V as extracted from various calculations of the intramolecular electron-phonon pairing in fullerenes [8]. V is related to the electron-phonon coupling constant λ via $V = \lambda/N_0$, where N_0 is the density of states at the Fermi level. The Fermi energy is set equal to $E_F = 0.25 \pm 0.05$ eV [13].

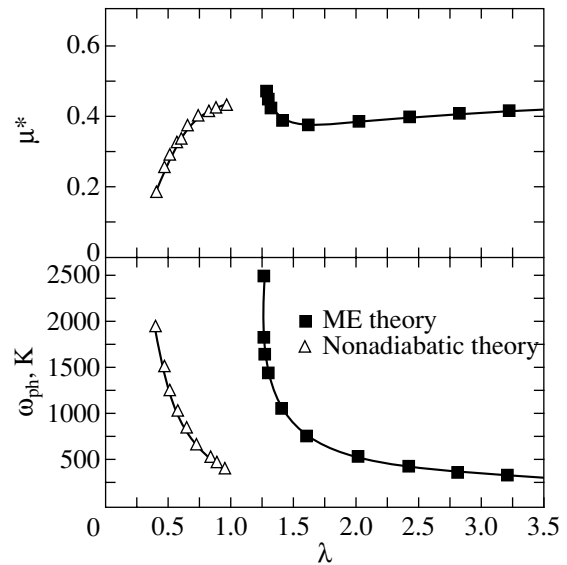


Fig. 2. Coulomb pseudopotential μ^* (upper panel) and phonon frequency ω_{ph} (lower panel) as a function of the electron-phonon coupling λ . Both the ME (filled squares) and nonadiabatic (open triangles) equations are solved in order to fit the experimental data $T_c = 30$ K and $\alpha_C = 0.21$.

squares), the Migdal parameter P is always larger than ~ 0.4 . This result is remarkably robust, and different shapes of the function $\alpha^2F(\omega)$ that eventually include contributions from the lowest intermolecular phonon modes always lead to $P > \sim 0.4$. We conclude, therefore, that the conventional phonon-mediated superconductivity is not a self-consistent picture of Rb_3C_{60} since the

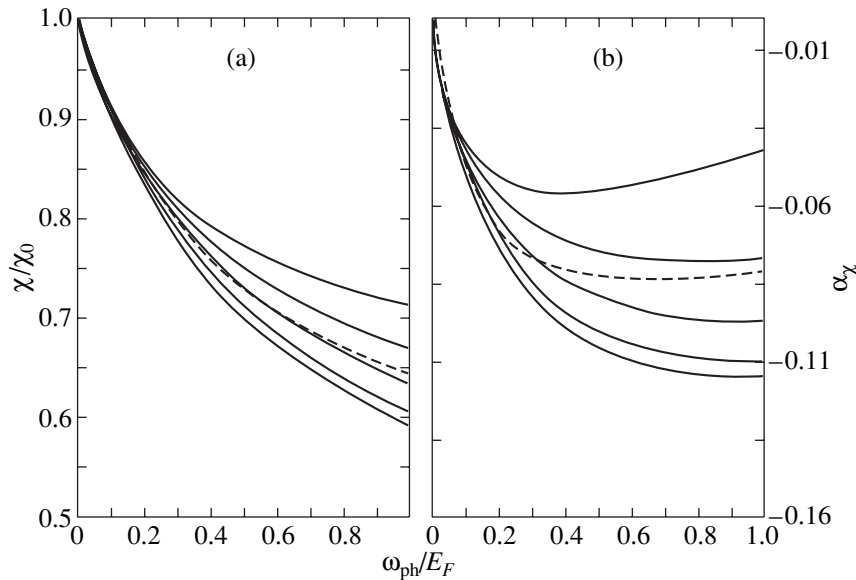


Fig. 3. (a) Nonadiabatic Pauli susceptibility and (b) its isotope coefficient as a function of the adiabatic parameter ω_{ph}/E_F for $\lambda = 0.7$. Dashed (solid) lines refer to the first- (second-) order nonadiabatic approximation (see text). From lower to upper solid lines: $Q_c = 0.1, 0.3, 0.5, 0.7,$ and 1.0 , respectively.

values of λ and ω_{ph} needed to fit $T_c = 30$ K and $\alpha_C = 0.21$ strongly violate Migdal's theorem [11].

The results of Figs. 1 and 2 imply that the description of superconductivity in C_{60} materials should be formulated beyond the ME theory. In particular, the low value of E_F suggests that the adiabatic hypothesis and Migdal's theorem should be abandoned from the start and that a consistent theory should be formulated by allowing ω_{ph}/E_F to have large values. In this perspective, in the past years, we constructed a theory of nonadiabatic superconductivity by explicitly including the vertex and other diagrammatic terms arising in the nonadiabatic regime [12, 13]. A primary role is played by the vertex diagrams, which have been shown to strongly depend on the exchanged phonon momentum and frequency \mathbf{q} and ω , respectively [13]. The momentum and frequency dependences of the vertex diagrams are quite complex, and it is hard, in principle, to determine in which way these nonadiabatic terms affect the superconducting properties, in particular, if they favor or disfavor the onset of superconductivity. In this regard, the microscopic characteristics of real materials are important. In particular, the strong degree of electronic correlation in fullerenes has been shown to have an important and positive effect in the nonadiabatic regime by favoring small \mathbf{q} scattering [14], the case where vertex corrections mainly enhance the superconducting pairing [12, 13]. In this context, the electron-phonon coupling λ no longer characterizes the strength of superconducting pairing, whereas the opening of new nonadiabatic channels of pairing appears to be the driving element of large critical temperatures. In simple words, this means that a moderate coupling λ , which, in

the context of the conventional adiabatic ME theory, is expected to yield no or low-temperature superconductivity, can actually account for large values of T_c in the new framework based on the nonadiabatic theory of superconductivity.

To illustrate this point, let us reconsider Rb_3C_{60} in the broader framework of nonadiabatic superconductivity. The open triangles in Fig. 2 are λ and μ^* values generated by numerical solutions of the nonadiabatic equations constrained to fit the experimental values $T_c = 30$ K and $\alpha_C = 0.21$ [11]. In order to model the strong correlation, we used an upper cutoff $q_c = 0.2k_F$ for the momentum transfer of the electron-phonon scattering (k_F is the Fermi momentum). The first remarkable difference between the ME theory (filled squares) and the nonadiabatic solutions (open triangles) is that much lower (and more realistic) values of λ are now needed to reproduce the experimental data. In nonadiabatic superconductivity, high values of the critical temperature arise from conventional values of λ ($\lambda < 1$) embedded in the new theory, rather than from extremely large values of λ ($\lambda > 1$) predicted by the conventional theory. It is also certainly worth stressing that the nonadiabatic solutions of Fig. 2 lead to values of P that are always less than ~ 0.25 [11]. This is perfectly compatible with the perturbative approach used, which disregards all nonadiabatic irreducible vertex diagrams of order P^2 and higher order terms.

At this point, it is significant to make a comparison between fullerenes and intercalated graphite compounds (GICs), for which quite low values of T_c are observed (for example, $T_c = 0.2$ K for K_8C). Supercon-

ductivity in GICs is explained by the weak-to-moderate (~ 0.3) coupling to carbon-phonon modes of energies close to those in C_{60} . Within the ME framework, some current theories claim that the enhancement of T_c as one goes from GICs to fullerides arises from an amplification of λ (from ~ 0.3 to ~ 1 or more) due to the finite curvature of the C_{60} molecule [15]. In the nonadiabatic model, instead, the most important difference between GICs and fullerides is the value of E_F . In the former compounds, in fact, E_F is of several electronvolts and Migdal's theorem holds true. Hence, in these terms, the increase in T_c as one goes from GICs to fullerides stems mainly from the opening of electron-phonon nonadiabatic channels rather than from a $\sim 300\%$ enhancement of λ .

The interpretation of superconductivity in C_{60} -based materials in terms of the nonadiabatic scenario can be sustained by the observation of clear additional fingerprints of such a nonadiabatic regime. In order to gain robustness, such fingerprints should be sought among those physical quantities for which some well-established properties in the ME regime are qualitatively modified in the nonadiabatic one. Let us consider, for example, the charge carrier mass m^* renormalized by electron-phonon interaction. In the ME regime, we have $m^* = (1 + \lambda)m$, where m is the bare mass. A strong prediction of the ME theory is that, since λ is independent of the ion mass M , no isotope effect is expected for m^* . Within the nonadiabatic model, the situation is completely different. Now, the electron self-energy is modified by the nonadiabatic vertex correction, so that m^* acquires an additional $\omega_{\text{ph}}/E_F \propto 1/M^{1/2}$ dependence, leading to a nonzero isotope effect on m^* . We found that, in general, the m^* isotope coefficient, $\alpha_{m^*} = -d\ln(m^*)/d\ln(M)$, is negative and that, for example, $\alpha_{m^*} \sim -0.2$ for $\omega_{\text{ph}}/E_F = 0.4$ and $\lambda = 1$ [16]. The experimental observation of nonzero values of α_{m^*} in fullerides would certainly imply a breakdown of the ME theory and strongly support the nonadiabatic picture.

Another measurable quantity which could unveil signatures of nonadiabaticity is the normal-state Pauli susceptibility χ . As pointed out by Fay and Appel [17], the lowest order electron-phonon correction to χ is a vertex diagram; thereby, the renormalization of the Pauli susceptibility is of the order $P = \lambda\omega_{\text{ph}}/E_F$. In the adiabatic regime, therefore, χ is expected to be unaffected by the electron-phonon interaction. Conversely, when P is no longer negligible, χ becomes dependent on λ and ω_{ph} , which can be detected using suitable experiments. We calculated the nonadiabatic effects on the Pauli susceptibility for different stages of perturbation theory in P ; the results are shown in Fig. 3 [18]. In the figure, the dashed lines refer to a simple ladder vertex correction, while the solid lines are results obtained including the second-order nonadiabatic terms for different values of the momentum cutoff $Q_c = q_c/2k_F$. For $P \rightarrow 0$, both approximation schemes lead to the ME

result $\chi = \chi_0 = 2\mu_B^2 N_0$, where μ_B is the Bohr magneton and N_0 is the density of states at the Fermi level. The first main result (Fig. 3a) is that, in the nonadiabatic regime ($P \neq 0$), χ is significantly reduced with respect to the adiabatic limit χ_0 . Hence, χ is no longer simply proportional to N_0 . This means that disregarding the electron-phonon coupling would lead to a substantial underestimation of the bare density of states as determined from spin susceptibility measurements as long as the system is in the nonadiabatic regime. A more striking consequence of the nonadiabatic effects on χ is that the Pauli susceptibility now becomes ion-mass dependent, which is reflected in its nonzero (negative) isotope coefficient $\alpha_\chi = -d\ln(\chi)/d\ln(M)$ (Fig. 3b). The observation of such an isotope effect, absent in the ME regime, represents a stringent test of the nonadiabatic hypothesis.

A further interesting qualitative difference between the ME and the nonadiabatic regimes is in the response of the superconducting state to disorder and nonmagnetic impurities. Within the adiabatic regime, isotropic s -wave superconductors are stable to the presence of weak disorder. In particular, T_c is nearly independent of the extent of disorder. This situation changes when we consider nonadiabatic superconductors [19]. In fact, the vertex corrections are quite sensitive to the extent of disorder, with the consequence that the effective nonadiabatic pairing is reduced. Therefore, for an s -wave superconductor in the nonadiabatic regime, disorder would reduce T_c , contrary to the expectations of the ME theory [19]. It is remarkable that a T_c reduction under ion irradiation has been recently reported for K_3C_{60} [5].

In summary, we have shown how the breakdown of Migdal's theorem and the opening of nonadiabatic channels identify the fulleride superconductors as nonconventional materials. The physics of such systems is largely governed by nonadiabatic interference effects, which are reflected in the anomalous behavior of observable quantities such as m^* , χ , and T_c . We believe that experiments in this direction are of great importance.

As a concluding remark, we think it interesting to add some considerations of the newly discovered superconductivity at $T_c = 39$ K in MgB_2 [7]. This material has a structure similar to that of GICs, with the boron atoms forming layers of two-dimensional honeycomb lattices. However, contrary to the GICs, the Fermi level crosses the in-plane σ bands, leading to a markedly two-dimensional character of the electronic properties. Moreover, the charge transfer of the intercalated Mg atoms is such that the σ bands are slightly doped with holes and the distance of the Fermi level crossing from the top of the band is only about 0.5 eV [20]. This feature, together with the high phonon frequency ω_{ph} of the boron atoms (up to 0.1 eV), indicates that MgB_2 could be in the nonadiabatic regime of the electron-phonon interaction. An additional interesting

point is that MgB_2 is far away from half-filling; in this case, it has been shown that the vertex corrections are, for the most part, positive, leading to enhanced pairing even in the absence of strong electron correlations [21]. Further analysis of the relevance of this hypothesis is currently under development.

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