Nonadiabatic superconductivity in fullerene-based materials

© C. Grimaldi, E. Cappelluti*, L. Pietronero*, S. Strässler

Département de Microtechnique — IPM, École Polytecnique Féderale Lausanne,
Lausanne, Switzerland
*Department of Physics, University "La Sapienza" and INFM,
Rome 1, Italy

Fullerene compounds have phonon frequencies up to $\omega_{\max} = 0.2\,\text{eV}$ and Fermi energy of order $E_F = 0.3\,\text{eV}$. 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 negligible *a priori* and that the conventional phonon-mediated theory of superconductivity does not longer apply. 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 provide several predictions on superconducting and normal state properties of fullerene compounds susceptible to be tested experimentally.

It is certainly due to their apparently ordinary phenomenology that superconductivity in C_{60} materials has been often 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 Fermi liquid-like normal state properties, order parameter of s-wave symmetry, sizeable carbon isotope effect, etc. [3]. However, despite of these reassuring properties, fullerene-based superconductors display also 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 ordinary ME framework, all these features tend to degrade superconductivity.

The recent discovery of superconductivity at $T_c = 52\,\text{K}$ in hole doped C_{60} [6] rises even more doubts on the validity of the ME picture. In fact, $T_c = 52\,\text{K}$ is the highest critical temperature among non-cuprates superconductors (it exceeds also $T_c = 39\,\text{K}$ 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 are degrading for a ME superconductor.

In addition to the above conceptual difficulties, there are actually several hints against the ME scenario disseminated in both experimental and theoretical published works on fullerides. 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 $\omega_{\min} = 400$ up to $\omega_{\max} = 2300\,\text{K}$. The relevant bandwidth for both electron and hole doped materials is $W = 0.5\,\text{eV} = 5800\,\text{K}$ so that for the A_3C_{60} half-filled compounds the Fermi energy is $E_F = 0.25\,\text{eV} = 2900\,\text{K}$ [3]. The value of E_F for the optimum hole doping ($T_c = 52\,\text{K}$) is even lower. Note that these are very small values compared to those of conventional superconductors for which E_F is of several eVs. A great effort has been devoted in the past to the calculation of the electron-phonon interaction in C_{60} materials. We summarize in Fig. 1 several published results on A_3C_{60} compounds obtained by 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 to the i-th phonon mode. Fig. 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 about 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 $\omega_{\text{ph}}/E_F \to 0$ 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 a first clue of the inadequacy of the ME theory of superconductivity in fullerides. Another important indication stems from the analysis of the experimental data of Rb_3C_{60} ($T_c = 30\,\text{K}$) for which only recently very accurate measurement of the carbon isotope coefficient $\alpha_{\text{C}} = -d\ln(T_c)/d\ln(M)$, where M is the isotopic carbon mass, has been available [9]. In fact, the measured value $\alpha_{\text{C}} = 0.21 \pm 0.012$ is sufficiently accurate to permit to test the consistency of the ME theory by estimating which values of the electron-phonon coupling λ, the phonon frequency ω_{ph} and the Coulomb pseudopotential μ^* are required to obtain the experimental values of T_c and α_{C} for Rb_3C_{60}. To this end, we have considered different models for the electron-phonon spectral function $\alpha^2F(\omega)$ and have numerically solved the ME equations by inserting the values of λ, ω_{ph}, and μ^* which reproduce the experimental data $T_c = 30\,\text{K}$ and $\alpha_{\text{C}} = 0.21$. 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 constant λ. For large values of λ, $T_c = 30\,\text{K}$ and $\alpha_{\text{C}} = 0.21$ are reproduced only for quite small phonon frequencies while decreasing λ quickly

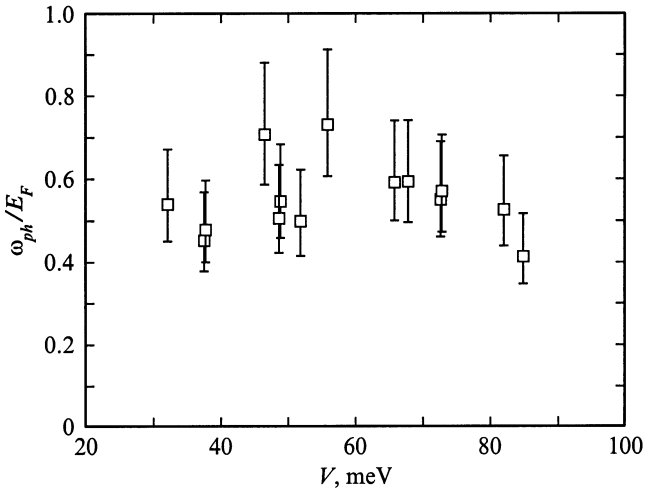

Figure 1. Adiabatic parameter $\omega_{\rm ph}/E_F$ versus the electron-phonon pairing interaction V as extracted from various calculations of the intramolecular electron-phonon pairing in fullerides [8]. V is related to the electron-phonon coupling constant λ via $V = \lambda/N_0$, where N_0 is the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

enhances $\omega_{\rm ph}$. 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 $\alpha^2F(\omega)$ and of the frequency cut-off in μ^*, we can lower the minimum allowed value of λ to about $\lambda_{\rm min} \approx 1.0$. Note that the obtained values of the Coulomb pseudopotential μ^* (upper panel, filled squares) are always quite large compared to the standart value $\mu^* \approx 0.1$ [10].

According to the ME analysis, Rb_3C_{60} is therefore an intermediate to strong coupling superconductor. Let us address now whether this conclusion is consistent or not with the ME framework [1,2,10]. As already 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 evaluating the order of magnitude P of the first nonadiabatic electron-phonon vertex correction. By following Migdal [1], P is given by

$$P = \lambda \frac{\omega_{\rm ph}}{E_F}. \qquad (1)$$

Conventional superconductors such as Pb, Al etc., have Fermi energies of order $E_F \sim 5-10$ 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 defined. To estimate the value of P in Rb_3C_{60}, we insert in Eq. (1) the value of λ and $\omega_{\rm ph}$ resulting from our solution of the ME equations. We obtain that for all couples of values λ, $\omega_{\rm ph}$ of Fig. 2 (lower panel, filled squares) the Migdal parameter P is always larger than about 0.4. This result is remarkably robust and different shapes of $\alpha^2F(\omega)$ which 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 values of λ and $\omega_{\rm ph}$ needed to fit $T_c = 30$ K and $\alpha_{\rm C} = 0.21$ 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 $\omega_{\rm ph}/E_F$ to have values sensibly larger than zero. In this perspective, in the past years we have constructed a theory of nonadiabatic superconductivity by including explicitly 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, respectively **q** and ω [13]. The momentum and frequency structure of the vertex diagrams is quite complex and it is hard in principle to determine in which way these nonadiabatic terms affect the superconducting properties, in particular if they favour or disfavour the superconductivity onset. In this regards 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 nonadiabatic regime by favouring small **q** scattering [14] where vertex corrections mainly enhance the superconducting pairing [12,13]. In this context, the electron-phonon coupling λ does no longer characterize the

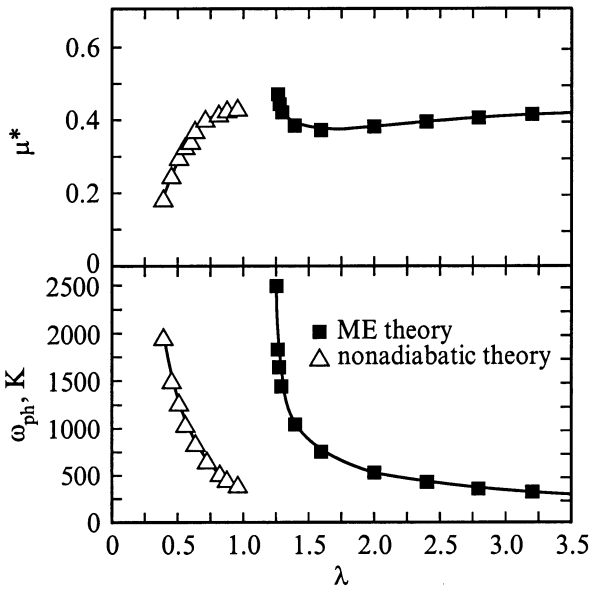

Figure 2. Coulomb pseudopotential μ^* (upper panel) and phonon frequency $\omega_{\rm ph}$ (lower panel) as a function of the electron-phonon coupling λ. Both the ME (filled squares) and the nonadiabatic (open triangles) equations have been solved in order to fit the experimental data $T_c = 30$ K and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

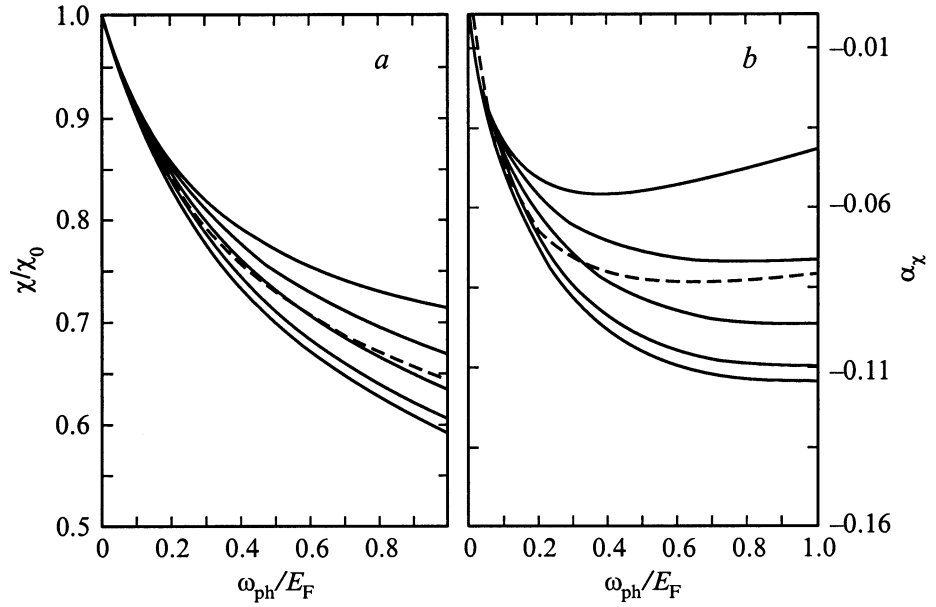

Figure 3. Nonadiabatic Pauli susceptibility (a) and its isotope coefficient (b) as a function of the adiabatic parameter ω_{ph}/E_F for $\lambda = 0.7$. Dashed (solid) lines refer to the first (second) order nonadiabatic approximation (see text). From lower to upper solid lines: $Q_c = 0.1$, 0.3, 0.5,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

strength of superconducting pairing whereas it is the opening of new nonadiabatic channels of pairing which 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 T_c's in the new framework on nonadiabatic theory of superconductivity.

To illustrate this point, let us re-consider Rb_3C_{60} under the broader framework of nonadiabatic superconductivity. The open triangles in Fig. 2 are the λ, μ^* values generated by the 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 have used an upper cut-off $q_c = 0.2k_F$ 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 the context of the nonadiabatic superconductivity, high critical temperatures arise thus from conventional values of λ ($\lambda < 1$) embedded in a 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 always less than ~ 0.25 [11]. This is perfectly compatible with the perturbative approach used, which disregard all the nonadiabatic irreducible vertex diagrams of order P^2 or larger.

At this point it is illuminating the comparison between fullerides and intercalated graphite compounds (GICs) for which quite low values of T_c are recorded (for example, $T_c = 0.2$ K for K_8C). Superconductivity in GICs is explained by a weak to moderate coupling ($\lambda \sim 0.3$) to carbon phonon modes of energies similar to those of C_{60}. Within the ME framework, some current theories claim that the enhancement of T_c from GICs to fullerides arises from an amplification of λ (from $\lambda \sim 0.3$ to $\lambda \sim 1$ or more) due to the finite curvature of the C_{60} molecule [15]. In the nonadiabatic framework, instead, the most striking difference between GICs and fullerides is the value of E_F. In the former compounds, in fact, E_F is of several eVs and Migdal's theorem holds true. Hence, in this perspective, the amplification of T_c 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 electron-phonon renormalized charge carrier mass m^*. In the ME regime $m^* = (1 + \lambda)m$, where m is the bare mass. A strong prediction of ME theory is that, since λ is independent of the ion mass M, no isotope effect is expected for m^*. Within the nonadiabatic framework, the situation is completely different. Now, the electron self-energy is modified by the nonadiabatic vertex correction so that m^* acquires and additional $\omega_{ph}/E_F \propto 1/M^{1/2}$ dependence leading to a non-zero isotope effect on m^*. We have 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 $\omega_{ph}/E_F = 0.4$ and

$\lambda = 1$ [16]. The experimental observation of non-zero values of α_{m^*} in fullerides would certainly imply the 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 some time ago by Fay and Appel [17], the lowest order electron-phonon correction to χ is a vertex diagram, so that the renormalization of the Pauli susceptibility is of order $P = \lambda\omega_{\rm ph}/E_F$. In the adiabatic regime, therefore, χ is expected to be unaffected by the electron-phonon interaction. Conversely, when P is no longer negligible, χ acquires a dependence on λ and $\omega_{\rm ph}$ which could be detected by suitable experiments. We have calculated the nonadiabatic effects on the Pauli susceptibility for different stages of a perturbation theory in P and 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 the results obtained by including the second order nonadiabatic terms for different values of the momentum cut-off $Q_c = q_c/2k_F$. For $P \to 0$, both approximation schemes reduce to the ME results $\chi = \chi_0 = 2\mu_B^2 N_0$, where μ_B is the Bohr magneton and N_0 is the density of states at the Fermi level. The first main result (Fig. 3, *a*) is that in the nonadiabatic regime ($P \neq 0$) χ is sensibly reduced with respect to the adiabatic limit χ_0. Hence, χ is no longer simply proportional to N_0. This means that disregarding the electon-phonon effects would lead to a substantial underestimation of the bare density of states from a spin susceptibility measurement as long as the system is in the nonadiabatic regime. A more striking consequence of the nonadiabatic effects on χ is that now the Pauli susceptibility acquires an ion mass dependence which is reflected in a non-zero and negative isotope coefficient $\alpha_\chi = -d\ln(\chi)/d\ln(M)$ (Fig. 3, *b*). 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 the response of the superconducting state to disorder and non-magnetic impurities. Within the adiabatic regime, isotropic *s*-wave superconductors are robust against the presence of weak disorder. In particular T_c is nearly independent of the amount of disorder. This situation changes when we consider nonadiabatic superconductors [19]. In fact, the vertex correnctions are quite sensitive to the amount of disorder in such a way 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 non-conventional materials. The physics of such systems is largely governed by nonadiabatic interference effects which are reflected in anomalous behaviors 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 is interesting to add some considerations on the newly discovered superconductivity at $T_c = 39$ 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 of the boron atoms ($\omega_{\rm ph}$ 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 and in this case it has been shown that the vertex corrections are mainly positive leading to an amplified pairing even in the absence of strong electron correlations [21]. Further analysis of the relevance of this hypothesis is currently under development.

References

[1] A.B. Migdal. Sov. Phys. JETP **7**, 996 (1958).
[2] G.M. Eliashberg. Sov. Phys. JETP **11**, 696 (1960).
[3] O. Gunnarsson. Rev. Mod. Phys. **69**, 575 (1997).
[4] Y.J. Uemura et al. Nature (London) **352**, 605 (1991).
[5] S.K. Watson et al. Phys. Rev. **B55**, 3866 (1997).
[6] J.H. Schön, Ch. Kloc, B. Batlogg. Nature (London) **408**, 549 (2000).
[7] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, J. Akimitsu. Nature (London) **410**, 63 (2001).
[8] M. Schluter et al. Phys. Rev. Lett. **68**, 526 (1992); M. Schluter et al. J. Phys. Chem. Solid **53**, 1473 (1992); J.C.R. Faulhaber et al. Phys. Rev. **B48**, 661 (1993); C.M. Varma et al. Science **254**, 989 (1991); V.P. Antropov et al. Phys. Rev. **B48**, 7651 (1993); N. Breda et al. Chem. Phys. Lett. **286**, 350 (1998).
[9] M.S. Fuhrer, K. Cherrey, A. Zettl, M.L. Cohen, V.H. Crespi. Phys. Rev. Lett. **83**, 404 (1999).
[10] J.P. Carbotte. Rev. Mod. Phys. **62**, 1027 (1990).
[11] E. Cappelluti, C. Grimaldi, L. Pietronero, S. Strässler. Phys. Rev. Lett. **85**, 4771 (2000).
[12] C. Grimadli, L. Pietronero, S. Strässler. Phys. Rev. Lett. **75**, 1158 (1995).
[13] L. Pietronero, S. Strässler, C. Grimaldi. Phys. Rev. **B52**, 10 516 (1995); ibid. **52**, 10 530 (1995).
[14] M.L. Kulic. Phys. Rep. **338**, 1 (2000) and references therein.
[15] P.J. Benning et al. Science **252**, 1417 (1991).
[16] C. Grimaldi, E. Cappelluti, L. Pietronero. Europhys. Lett. **42**,667 (1998).
[17] D. Fay. J. Appel. Phys. Rev. **B20**, 3705 (1979); ibid **22**, 1461 (1980).
[18] E. Cappelluti, C. Grimaldi, L. Pietronero. Phys. Rev. **B** (to be published).
[19] M. Scattoni, C. Grimaldi, L. Pietronero. Europhys. Lett. **47**, 588 (1999).
[20] J.M. An, W.E. Pickett. Phys. Rev. Lett. **86**, 4366 (2001).
[21] A. Perali, C. Grimaldi, L. Pietronero. Phys. Rev. **B58**, 5736 (1998).