# Nonadiabatic Channels in Fullerene Compounds

E. Cappelluti[1], C. Grimaldi[2], L. Pietronero[1] and S. Strässler[2]

*[1]Dept. Physics, University "La Sapienza", Rome, and INFM Roma1, Italy*
*[2]École Polytecnique Féderale Lausanne, DMT-IPM, Lausanne, Switzerland*

**Abstract.** The recent discovery of superconductivity with $T_c$ = 52 K in hole doped $C_{60}$ classifies the fullerene compounds among the highest-$T_c$ materials. Although there are strong evidences of a phonon based pairing in fullerenes, these anomalously high values of the critical temperature appear well beyond the electron-phonon upper limit of generally assumed to be 25-30 K. In addition, $C_{60}$ compounds are characterized by a small Fermi energy and a sensible degree of electronic correlation, all elements that usually disfavour the superconductivity onset. These considerations point towards a more exotic phonon-based superconductive pairing than the conventional BCS or Migdal-Eliashberg theory. We discuss this framework in the context of the nonadiabatic metal picture, where electron energies are comparable with phonon frequencies. In fullerene compounds high phonon frequencies range up to ≈ 2000 K whereas the Fermi energy is as small as 0.25 eV. As a consequence, we show that the electron dynamics stringly interferes with the lattice one leading to the breakdown of the Born-Oppenheimer principle and opening new nonadiabatic channels of interaction. Such interferences can disfavour or favour superconductivity, this latter case being realized in strongly correlated materials as fullerenes. Critical temperatures as large as 52 K, all together with other characteristic features, are naturally explained in the context of the nonadiabatic metal model.

The recent discovery of superconductivity in FET hole doped $C_{60}$ with $T_c$ = 52 K[1] has attracted renewed interest on superconductivity in fullerenes. A critical temperature as high as 52 K in these compounds is a quite puzzling feature. On one hand it exceeds the upper limit $T_c$ = 25-30 K considered as the maximum critical temperature achievable within the conventional Migdal-Eliashberg (ME) theory[2]. On the other hand such a high $T_c$ is in contrast with the extreme low density of carriers in these materials. Indeed, in the conventional framework a low carrier density implies small density of states and consequently low critical temperatures. The relevance of the low density of charge carriers in yielding high $T_c$'s has been pointed out by the Uemura's plot[3] which shows that high-$T_c$ materials, and in general all the "exotic" superconductors, are all characterized by having small densities of carriers. This observation suggests that new physics is induced in materials with few carriers.

However, notwithstanding the indications of an unconventional phenomenology, superconductivity in $C_{60}$-compounds is often described within the standard BCS of Migdal-Eliashberg (ME) framework. In that context, basic ingredients are large phonon frequencies $\omega_{\mathrm{ph}} \approx 2000$ K and a large electron-phonon coupling $\lambda \approx 1$, which should compensate the strong residual Coulomb repulsion $\mu^* \approx 0.4$[4]. The finite value of the isotope effect $\alpha = 0.21$[5] points also out a phonon based pairing, although its smallness suggests the presence of a significant $\mu^*$. High critical temperatures

CP591, *Electronic Properties of Molecular Nanostructures*, edited by H. Kuzmany et al.

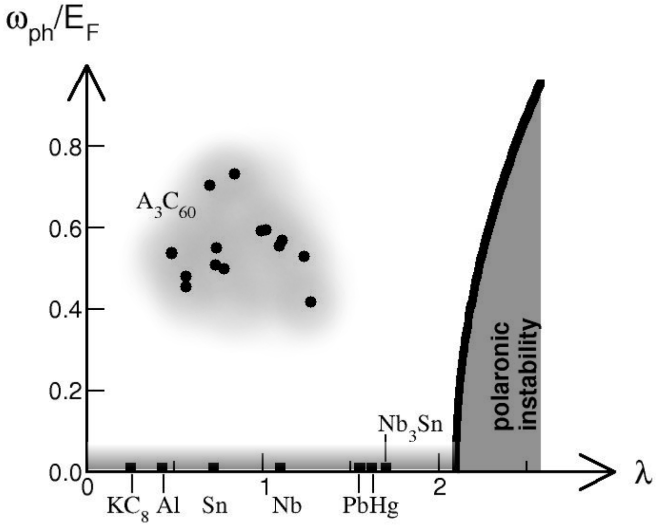

**FIGURE 1.** Phase diagram of conventional superconductors compared with the fullerene compounds in the space formed by the electron-phonon coupling $\lambda$ and the adiabatic parameter $\omega_{\mathrm{ph}}/E_F$. Data for the $A_3C_{60}$ family where taken from LDA, tight-binding, and *ab initio* calculations (Refs. [6-12]) by using standard values for the density of states $N(E_F)$ = 8 states / eV $C_{60}$ and for the Fermi energy $E_F$ = 0.25 eV.

are thus explained in terms of an extreme solution of ME theory, which appears quite unrealistic. In addition, as we are going to show, this standard scenario is intrinsically inconsistent with respect to the adiabatic problem, and a nonadiabatic approach is needed to properly describe superconductivity in fullerides.

A fundamental element characterizing fullerene compounds is indeed disregarded in the ME framework, namely the electron energy scale, parametrized by the Fermi energy $E_F$. Fermi energy, in both electron and hole doped materials, is typically of order 0.25 eV, comparable therefore with the highest phonon frequencies. In this situation, one of the basic assumptions of the conventional description of metals, namely the adiabatic Born-Oppenheimer principle, breaks down and the strong interplay between electron and lattice dynamics needs to be taken into account. Many features of the standard phenomenology of metals are thus deeply modified and the concept of nonadiabatic metal appears more useful to describe superconducting and normal state properties in nonadiabatic regime.

The degree of the failure of the adiabatic assumption can be parametrized by the adiabatic ratio $\omega_{\mathrm{ph}}/E_F$ which in $C_{60}$ based materials can be, as evident from the above discussion, as high as $\omega_{\mathrm{ph}}/E_F \approx 0.4\text{-}0.8$. The necessity of a novel nonadiabatic theory appears thus compelling, as shown by Fig. 1 where we have plotted the "adiabatic" phase diagram of conventional superconductors, including the graphite intercalated compound $KC_8$, and of the fullerene. All the conventional superconductors lie on the $\lambda$-axis, defined by zero adiabatic ratio. In contrast to that, fullerenes live in a totally different region of the phase diagram, characterized by large nonadiabatic effects. The figure also suggests a new route to search high-$T_c$ superconductivity in new materials. Indeed in 60s and 70s experimental search for high critical temperature superconductors moved mainly along the $\lambda$-axis, with the aim to look for stronger and stronger couplings. As discussed above, this search was intrinsically limited by the validity itself of the ME framework, as confirmed by the highest critical temperature $T_c \approx 23$ K achieved along this line in $Nb_3Ge$ thin films[13]. The large values of $T_c$ 's in $C_{60}$ materials instead appear directly related to nonadiabatic effects, considering even the moderate value of $\lambda$ in fullerenes compared with the larger $\lambda$'s of the conventional strong coupling superconductors. In particular, from Fig. 1 the adiabatic parameter $\omega_{\mathrm{ph}}/E_F$ results to be the driving ingredient of large critical temperatures in $C_{60}$ compounds and search for high-$T_c$ materials is suggested to move along the vertical axis of Fig. 1.

In order to understand on a microscopic ground in which way nonadiabatic effects can induce high critical temperatures, a more detailed analysis is needed. In this perspective in the past years we have constructed the theory of nonadiabatic superconductivity by explicitly including vertex and other diagrammatic terms arising in nonadiabatic regime[14-16]. A primary role is played by the vertex diagrams, which have been shown to highly depend on the exchanged phonon momentum and frequency, respectively $\boldsymbol{q}$ and $\omega$. 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 the 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 $\boldsymbol{q}$ scattering[17] where vertex corrections mainly enhance the superconducting pairing. In this context the electron-phonon coupling $\lambda$ does not characterize anymore the strength of superconducting pairing whereas it is the opening of new nonadiabatic channels of pairing which appears the driving element of large critical temperatures. In the simplest words, this means that a moderate coupling $\lambda$, 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 of nonadiabatic theory of superconductivity.

To illustrate this point, the concrete example of $Rb_3C_{60}$ can be useful since for this compound best experimental data are available. Recent measurements have indeed determined with the highest degree of accuracy the carbon isotope coefficient $\alpha = 0.21$[5], which, together with the large critical temperature $T_c \approx 30$ K, has been argued to be compatible with a ME scenario[5]. However, a more accurate analysis disproves this conclusion[18]. In Fig. 2 (left panel) we show a numerical solution of the ME equations with an Einstein phonon $\omega_0$ reproducing the experimental data of $Rb_3C_{60}$, namely $T_c = 30$ K and $\alpha = 0.21$. As we can see, in order to account for these experimental data with a phonon spectrum limited by the physically relevant phonon frequencies 300 K $\leq \omega_0 \leq$ 2000 K we need a unrealistically large electron-phonon coupling $\lambda \approx 1 - 4$. This extremely large value of $\lambda$ is already an indication of the failure of the conventional ME theory in describing superconductivity in fullerenes. Moreover one can test the intrinsic consistency of the ME solution by estimating the size $P$ of the nonadiabatic vertex corrections through the relation: $P \approx \lambda\omega_0/E_F$. The

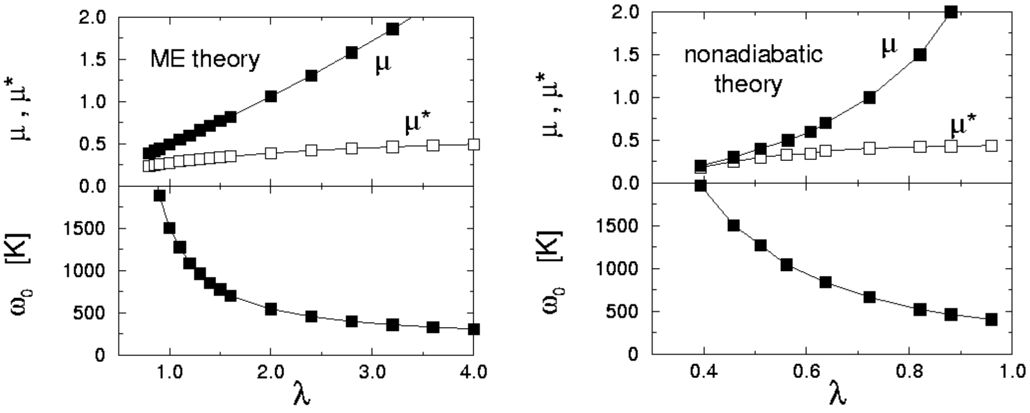

**FIGURE 2.** Left panel: electron-phonon coupling $\lambda$, phonon frequency $\omega_0$ and unscreened (screened) Coulomb repulsion $\mu$ ($\mu^*$) reproducing $T_c = 30$ K and $\alpha = 0.21$ in the adiabatic ME theory. Right panel: the same parameters evaluated in the nonadiabatic theory of superconductivity.

size of the vertex corrections corresponding to the ME solution in the left panel of Fig. 2 is shown to be always not negligible $P > 0.4$[18], pointing out the intrinsic inconsistency of the standard ME theory with respect to the adiabatic problem. This results does not depend on the particularly simple Einstein spectrum. Indeed, detailed calculations with different and realistic shapes of the electron-phonon coupling agree, even quantitatively, with the present analysis[19]. A nonadiabatic approach is thus needed. As we are going to show, the analysis of the same experimental data within the nonadiabatic theory provides a much more realistic description of the superconductivity in $Rb_3C_{60}$.

In the right panel of Fig. 2 we plot the microscopic parameters $\lambda$, $\omega_0$, $\mu$ and $\mu^*$ obtained within the nonadiabatic theory of superconductivity. For the relevant values of phonon frequencies the resulting electron-phonon coupling lies in a much more physical range $0.4 \leq \lambda \leq 1$, in good agreement with the numerical evaluations of $\lambda$ depicted in Fig. 1. In the context of the nonadiabatic superconductivity, high critical temperatures arise thus from conventional values of $\lambda$ embedded in a *new* theory, more than from extremely large values of $\lambda$ in a *conventional* theory[18]. The opening of new channels of interaction play therefore a crucial role in modifying the superconducting properties of nonadiabatic metals and in particular of fullerene compounds.

The nonadiabatic framework provides also a new scenario wherein unconventional features of both the superconducting and normal states acquire a natural explanation. For instance, a sensible suppression of the $T_c$ upon induced disorder and nonmagnetic impurities is predicted in nonadiabatic regime[20], in agreement with experimental data[21]. A finite isotope effect is also predicted to appear on quantities which in conventional ME theory are not expected to have it, as the effective electron mass $m^*$[22] and the Pauli spin susceptibility $\chi$[23]. The actual observation of it, by specific heat or magnetic susceptibility measurements, represents therefore a direct test on the relevance of nonadiabatic effects in fullerenes. In this respect the discovery of finite isotope effects on these quantities can be considered a trademark of nonadiabatic interaction and experimental work along this line is encouraged. A remarkable isotope effect on $m^*$ by penetration depth measurements has been actually observed in the underdoped region of the cuprates[24], suggesting a common origin of the high-$T_c$ pairing in both the materials.

In conclusion, we have revised the validity of the conventional ME theory of the superconductivity in fullerene compounds. We have shown that nonadiabatic effects are unavoidable in these materials due to the narrowness of the electron bands. A microscopic generalization of the superconductive equations in nonadiabatic regime points out the fundamental importance of the nonadiabatic interaction to account for the high values of $T_c$ and for a correct description of the superconducting and normal state properties.

## REFERENCES

1. Schön, J. H., Kloc, Ch., and Batlogg, B., *Nature* **408**, 549-552 (2000).
2. Allen, P. B., and Mitrovic, B., "Theory of Superconducting $T_c$," in *Solid State Physics,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull, New York: Academic Press, 1982,v. 37, pp. 1-92.
3. Uemura, Y. J. *et al*, *Phys. Rev. Lett.* **66**, 2665-2668 (1991).
4. Gunnarsson, O., *Rev. Mod. Phys.* **69**, 575-606 (1997).
5. Fuhrer, M. S. *et al*., *Phys. Rev. Lett.* **83**, 404-407 (1999).
6. Schluter, M. *et al*., *Phys. Rev. Lett.* **68**, 526-529 (1992).
7. Schluter, M. *et al*., *J. Chem. Phys. Solids.* **53**, 1473-1485 (1992).
8. Faulhaber, J. C. R., Ko, D. Y. K., and Briddon, P. R., *Phys. Rev. B* **48**, 661-664 (1993).
9. Varma, C. M., Zaanen, J., and Raghavachari, K., *Science* **254**, 989-992 (1991).
10. Antropov, V. P., Gunnarsson, O., and Liechtenstein, A. I., *Phys. Rev. B* **48**, 7651-7664 (1993).
11. Breda, N. *et al*., *Chem. Phys. Lett.* **286**, 350-354 (1998).
12. Onida, G., and Benedek, G., *Europhys. Lett.* **18**, 403-408 (1992).
13. There is a recent claim that superconductivity at $T_c \approx 40$ K in $MgB_2$ can be described in term of ME theory. However, the Fermi energy of the $\sigma$-bands involved in the superconductive order in this compounds is also quite small, $E_F \approx 0.5$ eV, and nonadiabatic effects are thus expected to be important even in this new kind of superconductor.
14. Pietronero, L., Strässler, S. and Grimaldi, C., *Phys. Rev. B* **52**, 10516-10529 (1995).
15. Grimaldi, C., Pietronero, L., and Strässler, S., *Phys. Rev. B* **52**, 10530-10546 (1995).
16. Grimaldi, C., Pietronero, L., and Strässler, S., *Phys. Rev. Lett.* **75**, 1158-1161 (1995).
17. Kulic, M. L., *Phys. Rep.* **338**, 1-264 (2000) and references therein.
18. Cappelluti, E., Grimaldi, C., Pietronero, L., and Strässler, S., *Phys. Rev. Lett.* **85**, 4771-4774 (2000).
19. Cappelluti, E., Grimaldi, C., Pietronero, L., Strässler, S., and Ummarino, G. A., preprint (2001).
20. Scattoni, M., Grimaldi, C., and Pietronero, L., *Europhys. Lett.* **47**, 588-594 (1999).
21. Watson, S., *et al*., *Phys. Rev. B* **55**, 3866-3869 (1997).
22. Grimaldi, C., Cappelluti, E., and Pietronero, L., *Europhys. Lett.* **42**, 667-672 (1998).
23. Grimaldi, C., and Pietronero, L., *Europhys. Lett.* **47**, 681-687 (1999).
24. Zhao, G. M., *et al*., *Nature* **385**, 236-239 (1997).