FAILURE OF THE MIGDAL-ELIAHBERG THEORY OF SUPERCONDUCTIVITY IN Rb$_3$C$_{60}$.

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We discuss the compatibility of the most accurate experimental data with the ordinary Migdal-Eliashberg theory of superconductivity in the fullerene compound Rb$_3$C$_{60}$. By using different model phonon spectra we conclude that the experimental data can be fitted only by invoking an electron-phonon coupling of order $\lambda \approx 3$. This exceedingly high value is unphysical and it is not consistent with the basic assumptions of the Migdal-Eliashberg theory. On the contrary, by relaxing the adiabatic hypothesis on which the Migdal-Eliashberg theory rests, the experimental data can be fitted by much more realistic values of $\lambda$. This generalized theory predicts also characteristic features absent in the Migdal-Eliashberg framework which can be experimentally tested.

1. Introduction

The critical temperatures of the fullerene compounds A$_3$C$_{60}$ (A=K, Rb, Cs, etc.) are the highest among the organic superconductors and compete in magnitude with those of some high-$T_c$ superconductors of the cuprate family. Moreover, if we compare $T_\text{c} = 0.2$ K of the graphite intercalated compound K$_8$C with $T_\text{c} = 19$ K of K$_3$C$_{60}$ or $T_\text{c} = 30$ K of Rb$_3$C$_{60}$, it becomes clear that fullerene compounds are genuine high-$T_c$ superconductors. In addition, as illustrated by the famous Uemura’s plot, the fullerene compounds, the high-$T_c$ cuprates, the heavy fermions, etc. belong to the same class of anomalous superconductors characterized by carrier concentrations two or three orders of magnitude smaller than those of conventional superconductors.

Despite of these evidences, it has become a common habit to regard the fullerene compounds as ordinary superconductors and to describe them in the framework of the usual Migdal-Eliashberg (ME) theory of superconductivity, just like the con-
conventional low-temperature superconductors Hg or Pb. Such an attitude has been certainly sustained by the relatively ordinary phenomenology of the normal and superconducting states compared to that of high-\(T_c\) cuprates. Among other things, the fullerene compounds lack in fact normal state pseudogaps, have an order parameter of \(s\)-wave symmetry and a sizeable isotope effect for the maximum \(T_c\). This point of view has led to interpret the high values of \(T_c\) in fullerene compounds in terms of a strong electron-phonon (\(e\)-ph) coupling \(\lambda\) generated mainly by intra-molecular phonon modes.

Such an interpretation is actually a quite heavy over-simplification of the problem and inevitably leads to the odd conclusion that, although these materials have extremely low carrier densities, may show transitions to ferromagnetic states, are close to a Mott-Hubbard transition, they are nevertheless the best ME superconductors known so far. This situation somehow resembles the one criticised by Anderson and Yu in connection with the A15 compounds and their attempts to interpret their superconducting states in terms of ordinary ME theory.

Here, we present evidences against the ME picture commonly advocated for the fullerene compounds. In particular, we show that the most accurate available experimental data on Rb\(_3\)C\(_{60}\) are clearly inconsistent with the ME theory of superconductivity. Moreover, we show also how all theoretical calculations of the \(e\)-ph interaction reported so far lead to results in contradiction with the adiabatic hypothesis which is at the basis of the ME framework. On the contrary, the relaxation of the adiabatic hypothesis leads to a more natural interpretation of the experimental data and defines a theory of nonadiabatic superconductivity which is more promising than the ME scenario to understand the fullerene compounds.

2. Breakdown of the Migdal-Eliashberg Theory

In the present discussion of the compatibility of the experimental data with the ME theory of superconductivity we refer solely to Rb\(_3\)C\(_{60}\). The reason is that only for this material sufficiently accurate data have become available. In fact, from both tunneling and infrared measurements, the ratio gap-\(T_c\) in Rb\(_3\)C\(_{60}\) has been measured to be \(2\Delta/T_c = 4.2 \pm 0.2\) and the most accurate measurements of the carbon isotope effect on \(T_c\) has led to \(\alpha_C = 0.21\), where \(\alpha_C = -d\log T_c/d\log M_C\) is the carbon isotope coefficient. As we show below, together with \(T_c = 30\) K this set of data permits to test the ME theory for Rb\(_3\)C\(_{60}\).

Let us begin by considering the following standard strong-coupling formulas derived from the ME equations:

\[
T_c = \frac{\omega_{in}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right],
\]

\[
\alpha_C = \frac{1}{2} \left[ 1 - \frac{1.04(1 + \lambda)(1 + 0.62\lambda)\mu^2}{(\lambda - \mu^*(1 + 0.62\lambda))^2} \right],
\]

\[
\frac{2\Delta}{T_c} = 3.53 \left[ 1 + 12.5 \left( \frac{T_c}{\omega_{in}} \right)^2 \ln \left( \frac{\omega_{in}}{2T_c} \right) \right].
\]
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where $\lambda = 2 \int \alpha^2F(\omega)d\omega/\omega$ is the $e$-$ph$ coupling, $\ln \omega_{in} = (2/\lambda) \int \ln \omega \alpha^2F(\omega)d\omega/\omega$ is the relevant phonon frequency and $\alpha^2F(\omega)$ is the $e$-$ph$ spectral function (also known as Eliashberg function). In equations (1) and (2) $\alpha^*$ is the Coulomb repulsive pseudopotential. Inserting the above reported experimental values of $T_c$, $\alpha C$ and $2\Delta/T_c$ in the left-hand sides of equations (1)-(3) completely determines the values of the three unknown microscopic parameters $\lambda$, $\mu^*$ and $\omega_{in}$ (for the moment we neglect the error bars of $\Delta$ and assume therefore $2\Delta/T_c = 4.2$). The unique solution is given by $\omega_{in} = 313$ K, $\mu^* = 0.43$ and $\lambda = 3.6$. Although the obtained values of $\omega_{in}$ and $\mu^*$ lie within a reasonable range of validity, the extremely large value $\lambda = 3.6$ is completely unrealistic. There are mainly two reasons for this conclusion. First, such a strong $e$-$ph$ interaction is expected to be source of lattice instabilities preventing the system to become superconductive. In fact, although the maximum allowed value of $\lambda$ compatible with superconductivity is not precisely known, it is generally believed that $\lambda \sim 1.5$ represents a reasonable upper limit. Instead this limiting value is largely surpassed by the ME solution $\lambda = 3.6$.

A second reason which makes $\lambda = 3.6$ incompatible with the ME theory is given by observation that the half-filled electron conduction bandwidth of Rb$_3$C$_{60}$ (as for the other fullerene compounds) is of order $W = 0.5$ eV. In this situation, the $e$-$ph$ vertex corrections which are completely neglected in the ME theory become important. In fact, the order of magnitude of the vertex corrections is roughly $\lambda\omega_{ph}/E_F$, where $\omega_{ph}$ is an averaged phonon frequency and $E_F$ is the Fermi energy. For conventional superconductors $\lambda\omega_{ph}/E_F$ is of order $10^{-3}$-$10^{-4}$ and the $e$-$ph$ vertex corrections can be safely neglected. Instead by using $\lambda = 3.6$, $\omega_{ph} \sim \omega_{in} = 313$ K and $E_F = W/2 \simeq 0.25$ eV, we obtain $\lambda\omega_{ph}/E_F \simeq 0.35$. This result reveals the inconsistency of the ME theory when applied to Rb$_3$C$_{60}$ since the vertex corrections, which should be negligible in the ME framework, turn out to be instead important.

The above analysis is confirmed also when, in place of the strong-coupling formulas (1)-(3), we solve numerically the ME equations to fit the experimental data $T_c = 30$ K, $\alpha C = 0.21$, and $2\Delta/T_c = 4.2 \pm 0.2$. In Fig.1 we report the calculated values of $\lambda$ for a $e$-$ph$ spectral function $\alpha^2F(\omega)$ schematized with a rectangle centered at $\omega_0$ and width $\Delta\omega_0$. For the whole range of $\Delta\omega_0/\omega_0$ values compatible with the vibrational frequencies of the fullerene molecule we obtain $\lambda \sim 3$, in agreement with the analysis based on the strong-coupling formulas. Also the calculated values $\omega_{in} \sim 350$ K and $\mu^* \sim 0.35$ are close to the values obtained above.

The above numerical evaluations of the ME equations confirm and strengthen therefore our conclusion that ME theory fails to describe superconductivity of Rb$_3$C$_{60}$. This situation is also supported by the various calculations of the $e$-$ph$ interaction in fullerenes reported so far. In Fig.2 we show a collection of data taken from various theoretical calculations of the $e$-$ph$ interaction $V = \lambda/N_0$, $N_0$ being the electron density of states per spin. The data refer to various calculations schemes including tight-binding, LDA, ab-initio etc. which estimate the coupling of the $t_{1u}$ electrons to the eight $H_g$ intra-molecular phonon modes. As it is apparent from the values reported in the abscissa, there is a large uncertainty in the value
Fig. 1. Electron-phonon coupling constant calculated from the solution of the ME equations for an Eliashberg function of rectangular form centered at $\omega_0$ and having width $\Delta \omega_0$. The ME equations have been solved by requiring to fit the experimental results $T_c = 30$ K, $\alpha_C = 0.21$, and $2\Delta/T_c = 4.2 \pm 0.2$.

Fig. 2. Adiabatic parameter $\omega_{ph}/E_F$ extracted from various calculations of the e-ph interaction in fullerenes. The average phonon frequency is calculated from $\omega_{ph} = \langle 1/\lambda \rangle \sum_i \lambda_i \omega_i$, where the index $i$ runs over the eight H$_g$ phonon modes with e-ph couplings and frequencies $\lambda_i$ and $\omega_i$, respectively. The Fermi energy is $E_F = 0.25 \pm 0.05$ eV.

of $\lambda/N_0$ which in fact results equally distributed between 32 meV and 85 meV, i.e. a variation of more than 100 %. However, despite of the serious disagreement on the value of $\lambda/N_0$, all these calculations agree in estimating the adiabatic parameter $\omega_{ph}/E_F$ to be larger than 0.4. In this case, Migdal’s theorem breaks down and the whole ME framework is invalidated. The reason for such high values of $\omega_{ph}/E_F$ stems from the fact that, independently of details, the H$_g$ phonons have energies ranging from 30 meV to 200 meV while the conduction $t_{1u}$ electron band has a width of only $W = 0.4 - 0.6$ eV so that $E_F = W/2 = 0.25 \pm 0.05$ eV and the electrons and phonons can have comparable energies.

3. Beyond Migdal’s Limit

The failure of the ME theory of fullerene compounds revealed from the analysis of both experimental (Fig.1) and theoretical (Fig.2) data suggests that the e-ph problem in these materials must be approached from a different perspective. From the above discussion, it is clear that the most natural starting point is to relax the adiabatic hypothesis on which the ME framework rests and consequently to generalize the theory to the nonadiabatic regime of the e-ph interaction. Within a perturbative scheme, this generalization means that nonadiabatic contributions such as e-ph vertex corrections must be included in the evaluation of both normal and superconducting state properties. A detailed derivation of such a generalized theory beyond Migdal’s limit has already been reported elsewhere. Here it is sufficient to remark that the nonadiabatic corrections are strongly dependent on the exchanged
phonon frequency \( \omega \) and momentum transfer \( q \) in such a way that for \( v_F q/\omega < 1 \) \((v_F q/\omega > 1)\) the resulting e-ph effective scattering is enhanced (diminished). As a consequence, the critical temperature \( T_c \) can be amplified by the nonadiabatic corrections if the e-ph scattering is mainly via small momentum transfer, as it is expected for strongly correlated systems and the weak screening due to the low charge carrier concentration.

Having a theory of nonadiabatic superconductivity available, let us now apply it to the situation of \( \text{Rb}_3\text{C}_{60} \). The evaluation of the zero temperature gap \( \Delta \) for nonadiabatic superconductors is a quite difficult task. However, there are various indications that the pseudopotential \( \mu^* \) is about 0.3. Let us consider therefore only the experimental data \( T_c = 30 \text{ K} \) and \( \alpha_{\text{C}} = 0.21 \), and fix the value \( \mu^* = 0.3 \). In this case, for a dispersionless phonon spectrum with frequency \( \omega_0 \), the ordinary ME equations lead to a unique solution with \( \lambda = 3.5 \) and \( \omega_0 = 300 \text{ K} \), very close therefore to the values obtained in the previous section. However, when we solve the generalized equations which include the nonadiabatic contributions, we find that for \( \mu^* = 0.3 \) the experimental data \( T_c = 30 \text{ K} \) and \( \alpha_{\text{C}} = 0.21 \) can be fitted by much more reasonable values of \( \lambda \). In Table 1 we report the results for different values of the dimensionless momentum transfer \( Q_c = q_c/2k_F \). The resulting e-ph coupling \( \lambda \) depends only weakly on \( Q_c \) and it is much lower than the unrealistically large values obtained by the ME analysis. In the last column of Table 1 we report also the values of \( \lambda \omega_0/E_F \) \((E_F = 0.25 \text{ eV})\) which provide a measure of the importance of the nonadiabatic corrections.

### Table 1

| \( Q_c \) | \( \lambda \) | \( \omega_0 \text{ [K]} \) | \( \lambda \omega_0/E_F \) |
|---|---|---|---|
| 0.1 | 0.46 | 1519 | 0.24 |
| 0.3 | 0.55 | 2340 | 0.44 |
| 0.5 | 0.76 | 1787 | 0.47 |

### 4. Discussion and Conclusions

The quite promising results on the experimental data of \( \text{Rb}_3\text{C}_{60} \) are solid arguments in favour of the nonadiabatic nature of the e-ph interaction in the fullerene compounds. Moreover, the nonadiabatic scenario is liable to be experimentally tested in different ways. Below we list the features we have identified to be characteristic of a nonadiabatic e-ph interaction and that cannot be displayed by a ME material:

(i) The critical temperature \( T_c \) is strongly suppressed by non-magnetic impurity scattering and the isotope coefficient acquires an anomalous dependence on disorder.

(ii) The normal state electron effective mass \( m^* \) becomes ion-mass dependent leading to a negative isotope coefficient of \( m^* \).
(iii) The normal state Pauli susceptibility $\chi$ acquires a dependence on the $e$-ph scattering. For $\omega_0/E_F \neq 0$, the e-ph interaction leads to a decreasing of $\chi$ with respect to the adiabatic limit $\omega_0/E_F \to 0$. Moreover, in analogy with $m^*$, $\chi$ has a nonzero negative isotope effect.

We note that the effect described in point (i) has been already observed in $K_3C_{60}$.

We conclude by stressing that experimental verifications of the predictions listed above is of primary importance to settle the degree of nonadiabaticity of the e-ph interaction in the fullerene compounds.

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