Strong-coupling effects in alkali-metal-doped C_{60}

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Various experiments indicate that K_3C_{60} and Rb_3C_{60} are in the strong-coupling regime. There is also both theoretical and experimental evidence for a large coupling of high-frequency intramolecular phonons with the electrons. If only these phonons are relevant, it is difficult to explain the relatively low T_c. This paradox can be resolved by introducing additional coupling with the low-lying intermolecular modes. Such a model also provides a consistent explanation of the tunneling experiments, and of the non-BCS behavior of the critical fields, penetration depth, and NMR relaxation time.

After the discovery[1] of superconductivity in alkali-metal-doped fullerenes, there are still open questions. Measurements of the isotope shift of T_c show that carbon phonons play a decisive role, although different groups report different numbers for the value of the shift. Several theoretical calculations (using rather different approaches) demonstrated large coupling with the high-frequency intramolecular phonons.[2–4] This is indirectly confirmed by the fact that these phonons change with the doping level and are altered by the superconducting transition (e.g., Ref. 5). In principle, the calculated coupling strength ($\lambda = 0.6 - 0.8$) is sufficient to explain critical temperature of 20–30 K. However, the hope that this model reflects all essential physics of the superconductivity in these compounds turned out to be premature.

An indication of that could already be seen in the calculations of Ref. 4: The calculated slope of T_c as a function of the lattice parameter is too steep in comparison with the experiment. Furthermore, it was shown[6] that the experimental dependence of T_c on the lattice parameter cannot be reconciled with the assumption that only intramolecular coupling influences superconductivity, as long as one takes the density-of-states dependence on the lattice parameter from the local-density approximation (LDA) calculations. [This dependence was later confirmed experimentally by NMR (Ref. 7) and magnetic susceptibility[8] measurements.] In fact, such a moderate dependence of T_c on the density of states normally appears when $kT_c/\hbar\omega_{ph}$ is about 0.05, which corresponds in this case to $\omega_{ph} \sim 300$ cm^{-1}.

Second, there is growing evidence that various characteristics of the superconducting state are strongly renormalized from their BCS values. One can mention here the results of magnetic measurements,[9,10] tunneling spectroscopy,[11] the absence of the Hebel-Slichter peak in NMR,[7] as well as the unusual temperature dependence of the penetration depth.[12] Strong coupling with hard intramolecular phonons should, however, result in much higher T_c's than those actually observed. Moreover, a careful analysis of the experimental data uncovers some problems within the strong-coupling BCS theory itself, even independent of the conclusions of Refs. 2–4 about the role of the intraband phonons.

The goal of this paper is to demonstrate that this apparent contradiction can be resolved if one assumes that besides the coupling with the intramolecular modes there is a considerable coupling with supersoft ($\omega \lesssim 40$ cm^{-1}) intermolecular phonons (hereafter we shall call this the two-peak model, TPM). The most likely candidates for this role are rotational vibrations of the C_{60} clusters, but acoustical or translational optical (K against C_{60}) phonons can also help. Neutron density-of-states measurements[13] show a clearly separated region at about 30 cm^{-1} which was interpreted as originating from intermolecular modes, so the starting point of the TPM is supported by the experiment. We shall show that all the above-listed problems can be quantitatively resolved within the frameworks of this model. The most important part of the TPM is that the electrons couple to two different bosons, whose characteristic energies differ by more than an order of magnitude. Since the most probable candidates for these roles are the intermolecular phonons with energies 3–4 meV and hard intramolecular phonons with average energy about 100 meV, we have

adopted for the numerical calculations the model Eliashberg function $\alpha^2F(\omega)$ shown in Fig. 1. The relative coupling strength was, somewhat arbitrary, chosen so that the first moments of the low- and high-energy parts of $\alpha^2F(\omega)$ have the ratio of 0.0086 (the first moment, also known as the electronic factor of the coupling constant, does not depend explicitly on the phonon spectrum, but only on the electronic structure and the electron-ion matrix element). For the value of the Coulomb pseudopotential we used $\mu^* = 0.3$ at the cutoff frequency, which was in the calculations about 6000 cm^{-1}. For the sake of simplicity we shall also assume that the effect of pressure or doping manifests itself only via the density of states and can be simulated by a homogeneous scaling of $\alpha^2F(\omega)$. All numerical results discussed below were obtained by solving numerically the Eliashberg equations with this $\alpha^2F(\omega)$.

Let us start with the critical temperature. As a first approximation, one can use the McMillan formula

$$kT_c = \frac{\hbar\langle\omega_{\log}\rangle}{1.2}\exp\left(\frac{-1.04(1+\lambda)}{\lambda-\mu^*-0.62\lambda\mu^*}\right), \quad (1)$$

where μ^* is the Coulomb pseudopotential at $\langle\omega_{\log}\rangle$ (the logarithmically averaged phonon frequency). As mentioned above, the McMillan formula can provide a reasonable description of the dependence of T_c on the density of states, as long as one assumes that $\lambda = 1 - 1.2$ and $\langle\omega_{\log}\rangle \simeq 300$ cm^{-1}. The problem is that all intramolecular phonons have higher frequencies, most of them much higher, so $\langle\omega_{\log}\rangle \simeq 300$ cm^{-1} seems to be incompatible with any model which assumes an intramolecular origin for superconductivity. In the case of two well-separated peaks in $\alpha^2F(\omega)$, $\langle\omega_{\log}\rangle$ is simply $\omega_1^{\lambda_1/\lambda}\omega_2^{\lambda_2/\lambda}$. If we take for the intermolecular phonons frequency $\omega_1 \simeq 40$ cm^{-1}, and for the intramolecular phonons frequency $\omega_2 \simeq 1000$ cm^{-1}, then in order to obtain $\langle\omega_{\log}\rangle \simeq 300$ cm^{-1} one needs to assume that $\lambda_1/\lambda_2 \simeq 0.6$. However, it is well known that the phonons with the frequency $\hbar\omega < 2\pi kT_c$ are very inefficient for raising T_c, and the McMillan equation becomes invalid for such modes (see, e.g., Ref. 14). In K_3C_{60} $2\pi kT_c$ corresponds to about 80 cm^{-1}, and in Rb_3C_{60} to about 130 cm^{-1}. We see that in both cases it is much larger than ω_1, so, presumably, λ_1/λ_2 must be much larger than the McMillan estimate above. Indeed, the spectral function shown in Fig. 1 has $\lambda_1/\lambda_2 = 2.7/0.5 = 5.4$, and this ratio provides the correct dependence of T_c on λ (λ for K_3C_{60} would be in this case about 2.6, and for Rb_3C_{60} about 3.3). Furthermore, it is likely that λ_1 is dependent not only on the density of states, but also directly on the lattice parameter; λ_2 is most probably simply proportional to the density of states. So, we see that the dependence of T_c on the lattice parameter can be easily understood in the framework of the TPM.

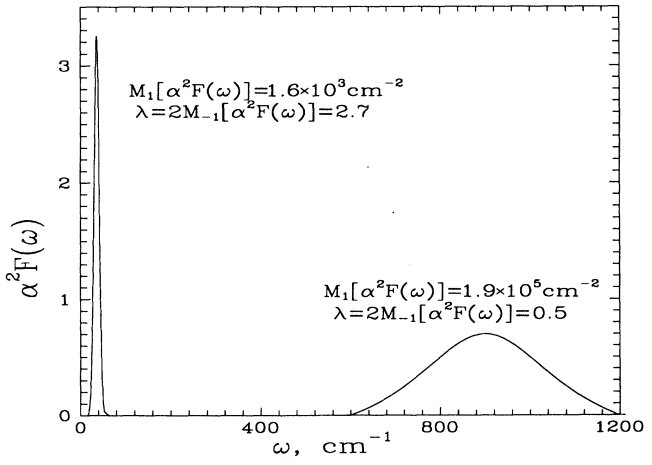

FIG. 1. Model spectral function used for the numerical solution of the Eliashberg equations. The coupling constants λ and the first moments of $\alpha^2F(\omega)$ (in 10^4 cm^{-2}) for the two parts of the spectrum are also shown.

Let us now turn to the superconducting gap. At the moment only one tunneling experiment[11] has been reported, with $2\Delta/kT_c = 5.3 \pm 0.2$ and 5.2 ± 0.3, for K_3C_{60} and Rb_3C_{60}, respectively. In the usual theory (one peak) $2\Delta/kT_c \gtrsim 5$ corresponds to $\lambda \gtrsim 2.54$. Another striking result is that the dependence on T_c, if any, seems to be opposite to what one would expect from the usual theory. The TPM can easily explain not only the large reduced gap, but also its independence from T_c. The enhancement of the reduced gap in the strong-coupling regime is due to the fact that the thermally excited phonons suppress the superconductivity, so that the actual transition temperature is lower than the one expected in the BCS model. This pair-breaking effect increases with the number of the thermally excited phonons, so that, first, the soft phonons are more efficient than the hard ones, and, second, $2\Delta/kT_c$ increases with T_c (see, e.g., review in Ref. 14). However, the phonons with $\hbar\omega \lesssim \pi kT_c$ are static defects, from the point of view of the Cooper pairs, so they cannot break the pairs. In the TPM that we use the low-energy phonons have energy from 20 to 50 cm^{-1}, corresponding to 30–70 K. As a result, when T_c becomes larger than 20–25 K, $2\Delta/kT_c$ start to decrease. In accordance with this picture, our calculations of $2\Delta/kT_c$ in the TPM give a nonmonotonic behavior with the maximum of about 5.3 (Fig. 2) at $\lambda \approx 2.9$ ($T_c \approx 23$ K). There are also many indirect indications of a strong coupling in K_3C_{60} and Rb_3C_{60}. One of those has been pointed out in Ref. 10, using the fact that in the Ginzburg-Landau theory the slopes of the critical fields H_{c1} and H_{c2} at T_c are uniquely related to the specific-heat jump. Using the data of Holczer *et al.*[15] for K_3C_{60} we have calculated $\Delta C/T_c = 380$ mJ/mole K^2. Analogous calculations for Rb_3C_{60}, based on the measurements of Politis, Sokolov, and Buntar[16], give $\Delta C/T_c = 300$ mJ/mole K^2. The measurements of Sparn *et al.*[17] give $\Delta C/T_c = 230$ mJ/mole K^2. This can be compared to the BCS values [$\Delta C/T_c = 9.41k_B^2N(E_F)$], which are, if one uses the LDA values for $N(E_F)$ calculated by Satpathy *et al.*,[6] 49 and 57 mJ/mole K^2, respectively. The renormalization from the BCS value is therefore 7.8 for K_3C_{60} and 5.3 or 4.0 for Rb_3C_{60}. One should be cautious about these numbers, because of the experimental difficulties in measuring $H_{c1}(T)$, but one can still

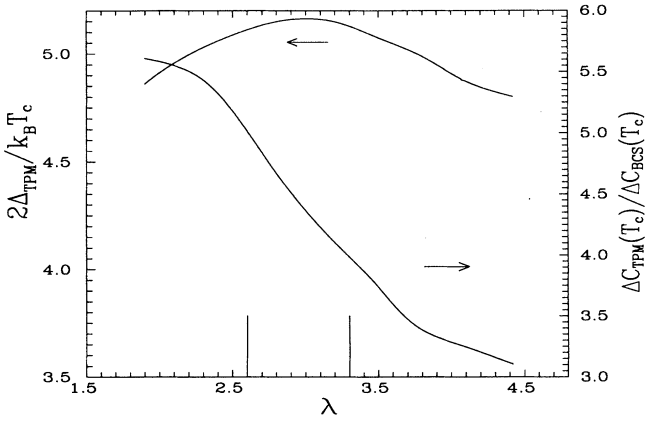

FIG. 2. Reduced gap parameter (upper line) and the renormalization factor for the specific-heat jump (lower line) in the two-peak model. The values of λ corresponding to $T_c \approx 20$ K (K_3C_{60}) and to $T_c \approx 30$ K (Rb_3C_{60}) are marked.

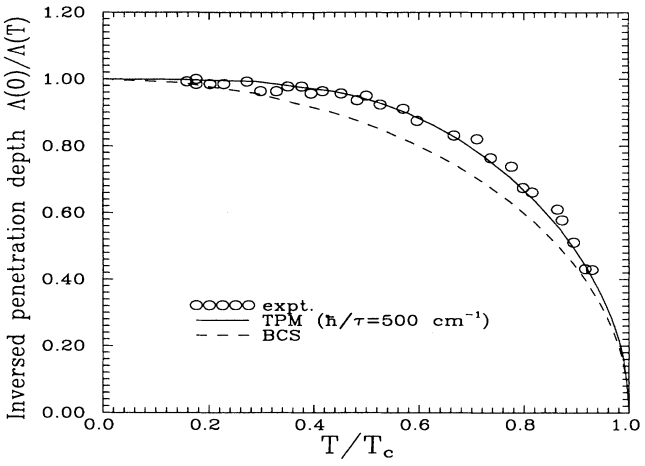

FIG. 4. The same as Fig. 3 but for the inversed penetration depth. Experimental points (μSR) for Rb_3C_{60} are from Ref. 12.

conclude that the renormalization is very strong, and at least as strong for K_3C_{60} as for Rb_3C_{60}, if not stronger. The renormalization of the specific-heat jump is naturally related to the renormalization of the gap, so we can expect our TPM model to provide a reasonable explanation of this also.[18] The numerical calculations (Fig. 2) confirm this expectation: the calculated values are 5.0 and 4.0 for K_3C_{60} and for Rb_3C_{60}, respectively.

Another important observation[9] is that the upper critical field does not saturate with cooling below at least $0.2T_c$. As discussed in Ref. 9, there can be several mechanisms for that, but it seems they can explain only about one half of the observed deviation from the BCS behavior. It is well known that the strong-coupling effects increase H_{c2} at low temperature. We have calculated $h_{c2}(T) = H_{c2}(T)/(T-T_c)H'_{c2}(T_c)$ in TPM (Fig. 3), and found that the difference between the experimental and the BCS behavior can be explained in this way. We have used the value 500 cm^{-1} for the relaxation frequency according to the resistivity estimate of 4 mΩ cm, and in order to estimate the effect of the Pauli limiting we have used the value 1.7×10^5 m/sec, according to band-structure calculations.[6] The corresponding mean free path is about 25 Å. Another observation is that the penetration depth, measured by muon relaxation technique,[12] increases with T faster than $1/(1-T^2/T_c^2)^{1/2}$, in contrast to the BCS model. Such behavior was also observed in the high-T_c cuprates, where it was attributed to the strong-coupling effects.[19] We have checked that the TPM can explain this, and found good agreement with the experiment (Fig. 4).

The last point that we want to emphasize is the absence of the Hebel-Slichter peak in the NMR (Ref. 7) data. Scattering from thermally excited phonons is known to be able to smear out this peak completely.[20] This actually happens in the TPM, as shown in Fig. 5 (calculations were done for the coupling strength cor-

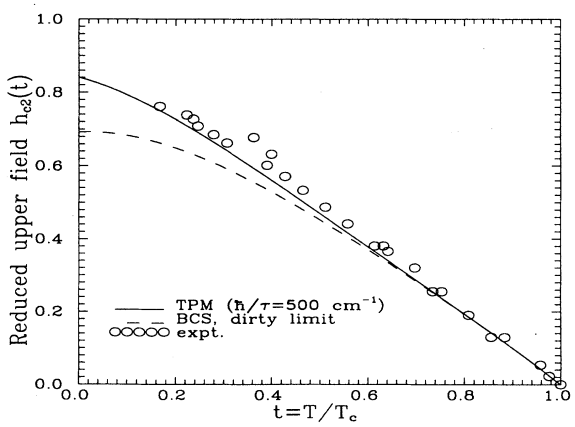

FIG. 3. Reduced upper critical field in the two-peak model (relaxation frequency $1/\tau = 500$ cm^{-1}, $\lambda = 3.3$) and in the dirty weak-coupling (BCS) limit. Experimental points for K_3C_{60} are from Ref. 9.

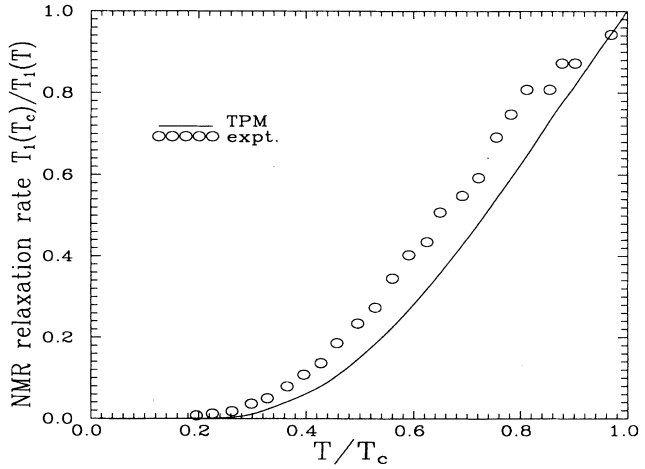

FIG. 5. The same as Fig. 3 but for the NMR relaxation rate. Experimental points for Rb_3C_{60} are from Ref. 7

responding to Rb_3C_{60}), so it provides an explanation of this effect, too. Furthermore, at low temperatures, the relaxation rate is determined not by the value of the superconducting gap, but mostly by the finite (in the strong-coupling regime) density of states inside the gap. The latter is, roughly speaking, proportional to the number of real phonons, so that the temperature dependence at small T follows the Arrhenius law although not with the exponent $\Delta/kT \simeq 2.5T_c/T$, but with $1.9T_c/T$. [The number of the thermal phonons is approximately $(\exp -50K/T)$]. This explains why the reduced gap extracted from NMR,[7] ($2\Delta/T \simeq 4$ for Rb_3C_{60}) is substantially smaller than that measured by tunneling.

To summarize, we have shown that, although it seems hardly possible to explain the existing experimental information about superconducting fullerenes either by the electron-phonon coupling with hard intramolecular phonons only, or by a strong coupling with any other excitations, one can easily explain essentially all existing experiments by adopting a two-peak model, where electrons couple both to the hard intramolecular vibrations and to the very soft intermolecular phonons. The relative coupling strength, in terms of the first moment of the Eliashberg function, that is needed to achieve a good numerical agreement with the experiment, is less than 1% for the soft part. It should be noted that nonadiabatic (non-Migdal) effects which can exist in C_{60} were not taken into account, but we believe that the above consideration will be qualitatively correct in this case too.

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