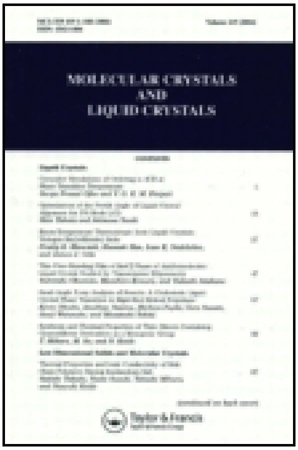

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High TC and Narrow Band in Fullerenes: The Anderson Paradox

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HIGH TC AND NARROW BAND IN FULLERENES : THE ANDERSON PARADOX

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Abstract : High Tc superconductors all have their Fermi level in the middle of a high peak of the density of states (DOS). This explains the value of λ, but is not enough to explain their high critical temperature : high DOS is usually associated with a narrow band width, which, as shown by Anderson, prevents the renormalization of μ into μ^*, thus diminishing or suppressing Tc. Usually, a sufficient normalisation is still possible since the peak is set on a broader band. We calculated the Tc for compounds of the C_{60} family: the basis of the peak is not very broad, but the neighbouring bands are very rich in electrons and help the renormalization. The results are in good agreement with experiments. The model also explains the variation of Tc with applied pressure and the discrepancy between the measured value of the coherence length and the expected value obtained from the Fermi velocity.

I INTRODUCTION

Carbon 60 is a highly symmetric molecule, composed of 60 carbon atoms at the vertices of a truncated icosahedron with 20 hexagonal faces and 10 pentagonal faces. It is much in the like of a soccer ball. It solidifies in the f.c.c. system, thus leaving 1 octahedral and 2 tetrahedral empty sites per unit cell. These are partly filled when the solid is doped with a metal. The compound formed with heavy alkaline metals are of great interest : they are superconducting with a critical temperature *Tc* ranging from 18 K for K_3C_{60},up to 30 K and more for Rb_3C_{60} and for $CsRb_2C_{60}$.

II. ELECTRONIC STRUCTURE

A first step in the understanding of superconductivity is the knowledge of electronic band structure.The band will be formed from the C_{60} molecular orbitals. The lowest unoccupied orbital (LUMO) in C_{60} is three fold degenerate. Each K atom will give an electron to occupy this orbital. So K_3C_{60} corresponds to a half occupied conduction band, which gives rise to a metallic behaviour. Since the energy of the electronic level for potassium is significantly higher than for C_{60}, this electron transfer is almost complete and K_3C_{60}, although metallic, is an ionic compound. This ionic character has been established by saito and al [12] Molecular orbitals overlap strongly but not as strongly as the carbon orbitals do, so that each of them gives rise to a narrow band. More particularly the LUMO of C_{60} becomes a conduction band, well separated in energy from the other bands, about 0.5 eV large, with a sharp peak in the middle more than 10 states/eV.C_{60} high, near which the Fermi level is to be found for K_3C_{60}.

Figure 1 summarizes all of this. More details about electronic structure can be found in Hebard [1], Freeman [2], and Saito [3].

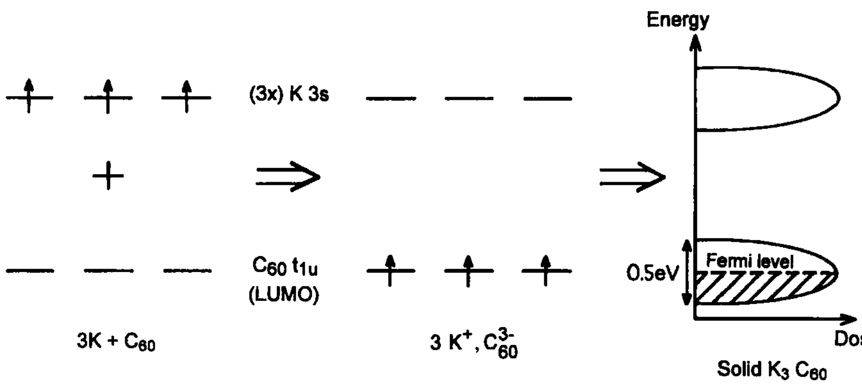

FIGURE 1 : Schematic of simplified electronic structure formation for K_3C_{60} showing only K HOMO et C_{60} LUMO.

III SUPERCONDUCTIVITY

Very often high Tc is attributed to the conjunction of the very high density of state in the peak near the Fermi level and of an exceptionally high Debye temperature for K_3C_{60} compared to ordinary metals or alloys.It is indeed possible to calculate values for λ, the electron phonon coupling from electronic structure and to find good evaluations of the critical temperature (see for instance Freeman [2]).

Nevertheless, these calculations usually show the same flaw with few exceptions [7] : They do not take into account the electronic repulsion μ (or its renormalized value μ^*) or fail to explain the value they choose for it. This is all the more worrying since Anderson [4] showed 30 years ago that μ plays a crucial part in superconductivity : for reasons of stability of the material, μ must be slightly higher than λ. This would never allow for superconductivity if μ was not renormalized in μ^* by the fact that electron-electron interactions have a far greater range in energy (of the order of E_f, the Fermi energy) than the electron phonon interaction (of the order of $\hbar\omega_D$ were ω_D is characteristic of the phonon frequency). Typically one has :

$$\mu^* = \frac{\mu}{1 + \ln \frac{E_f}{\hbar\omega_D}} \approx \frac{\mu}{5} \text{ , and}$$

$$T_C = 1.14\,\hbar\omega_D \exp \frac{1}{\lambda - \mu^*}$$

Of course the narrower the band, the poorer the renormalization. As a consequence it is usually admitted that narrowing the conduction band though increasing λ will decrease *Tc* and that a narrow-band system can not be superconducting at all.

The purpose of this article is to evaluate μ^* within the Morel-Anderson [4] framework, and to show that high *Tc* is possible in fullerenes with a BCS mechanism. Inspired by our previous work on cuprates [5] we shall show how a relatively narrow peak can still lead to renormalized value for μ when we take into account its broader base and the influence of the neighbouring bands.

IV CALCULATION

The principle of the calculation has been explained previously [4] [5]. Its main difference with Anderson and Morel method is the fact that, being near a peak of the density of states (DOS) we do not (we can not) consider, that this density is constant. We replace the density at the Fermi level used in the BCS theory by a density function of the energy. To simplify calculation, however we took this DOS to be triangular-shaped, which seems to be the simple shape the most like to the real DOS. We also modelize the other bands with triangles.

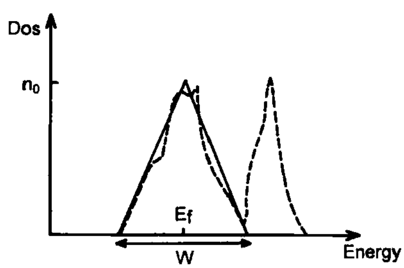

FIGURE 2 : Broken line : conduction band of K_3C_{60} (from ref. [1]) ; Solid line : approximation by a triangle of variable height n_0 and of base W, determined so as to have 3 (orbital) states/C_{60}.eV for the whole band. The other bands are also modelized by triangles of same height, at energy E_i from the Fermi level and of width W_i, chosen to have the correct number of states in the band.

We start from the self consistent equation for $\Delta_{\vec{k}}$

$$\Delta_{\vec{k}} = -\sum_{\vec{k}'} V(\vec{k}-\vec{k}') \frac{\Delta_{\vec{k}'}}{2\sqrt{\varepsilon_{\vec{k}'}^2+\Delta_{\vec{k}'}^2}} \tanh \frac{\sqrt{\varepsilon_{\vec{k}'}^2+\Delta_{\vec{k}'}^2}}{2k_B T},$$

which around Tc becomes:

$$\Delta_{\vec{k}} = -\sum_{\vec{k}'} V(\vec{k}-\vec{k}') \frac{\Delta_{\vec{k}'}}{2\left|\varepsilon_{\vec{k}'}\right|} \tanh \frac{\varepsilon_{\vec{k}'}}{2k_B T_c}$$

Here we make an important assumption (previously introduced by BCS [6], Morel and Anderson [4] and Friedel and Labbé [7] : we take $V(\vec{k}-\vec{k}')$ to be the sum of two constant terms :

the electron-phonon interaction,

V_p if $\left|\varepsilon_{\vec{k}}\right|$ and $\left|\varepsilon_{\vec{k}'}\right| \leq \hbar\omega_D$

0 otherwise,

the electron-electron interaction

V_C if $\left|\varepsilon_{\vec{k}}\right|$ and $\left|\varepsilon_{\vec{k}'}\right| \leq \frac{W}{2}$

0 otherwise

By summing along constant energy surfaces in equation (3) it is possible to replace the sum over $\vec{k}'$ by an integral over the energy thus introducing the density of state $n(\varepsilon)$ (see fig. 2). Solving this equation as in ref. [5] gives a result for Tc :

$$T_c = 1.14 \frac{\hbar\omega_D}{\exp\frac{2\hbar\omega_D}{W}} \exp\frac{-1}{\lambda-\mu^*} \quad \text{with}$$

$$\mu^* = \frac{\mu}{1+\mu\left[\ln\frac{W}{2\hbar\omega_D}+\frac{2\hbar\omega_D}{W}-1+\sum F(E_i, W_i)\right]} \quad \text{where}$$

$$F(E, W) = \frac{1}{2}\left(\ln\frac{E+W/2}{E-W/2}+\frac{2E}{W}\ln\frac{E^2-W^2/4}{E^2}\right)$$

The renormalization is effective because the adjacent bands contain a great number of electronic states.

V COMPARISON WITH EXPERIMENT

To calculate values for Tc we have taken the evaluation for λ computed by Freeman [2] (see fig. 3) for different C_{60} compounds doped with K, Rb and Cs. The linear dependence of λ in n_0 may seem surprising, but can be explained by a factorisation of $\lambda = n(E_f)\, V_p$ in two quantities, $n(E_f)$ the density of state which depends only on *extra ball* parameters (the distance between balls) and V_p , the electron-phonon interaction, which depends only on *intra ball* quantities (the phonon modes of C_{60}) [6].

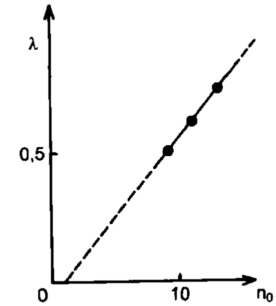

FIGURE 3 : λ versus n_0 (states/C_{60}.eV), adapted from ref. [2]

For the sum of the $F(E_i, W_i)$ we took into account the three nearest bands above and under the conduction band (in a range of -3 eV to +3 eV). We find a value for the sum varying from 1.0 for K_3C_{60} to 0.7 for Cs_3C_{60}. We replaced these values by a linear fit in $1/n_0$.

We took $\mu = \lambda$, $\hbar\omega_D$=1100 K [2] and calculated Tc. Fig. 4 shows its value as a function of the maximal DOS n_0. It should be noted however that only the first part of the curve (about n < 20) is numerically accurate, for higher values of n_0 the extrapolation on the value of λ is hazardous, and the calculation of Tc starts to rely on a strong coupling scheme we did not study. Yet the idea of the increase of λ competing with a decrease of renormalization remains valid. The maximum of the curve should still exist, but appears for a lower n_0, at a lower temperature. Fig. 5 shows a comparison with experiments of different origins. We can see that our model is in rather good agreement with experiment, considering the fact it is very simple.

This model also explains the variation of the critical temperature with applied pressure : As pressure is applied, C_{60} molecules are closer to one an other, and their overlap increases. Therefore the band becomes larger, the DOS diminishes and Tc is reduced.

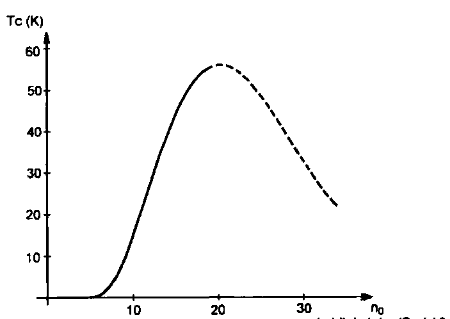

FIGURE 4 : Tc versus n_0. Only the solid part of the line is to be taken as significant.

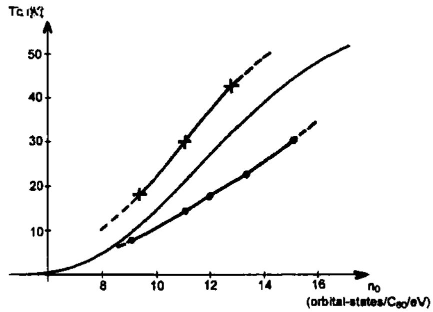

FIGURE 5 : Tc versus n_0 : solid line : our calculation ; crossed line : results from ref. [2] (Freeman) ; circled line : results from ref. [8], obtained upon applying pressure on K_3C_{60} and Rb_3C_{60}.

We also made other calculations on the same model, but using a different band structure, made of the superposition of two flat (rectangular) structures the larger, of width W and height n_0 simulating the width of the band, the smaller, of width D (D> $\hbar\omega_D$) and height n_0 simulating the peak on the top of the other one. The total number of electrons is still 6 e^-/unit cell. Through the same process as above we obtain the same expression for Tc but with a different expression for μ^* :

$$\mu^* = \frac{\mu}{1 + \mu\left[\frac{n_0}{n_0+n_1}\ln\frac{W}{2\hbar\omega_D} + \frac{n_1}{n_0+n_1}\ln\frac{D}{2\hbar\omega_D}\right]}$$

The result obtained, though similar to the triangular shaped, gives a less satisfying fit. Nevertheless, this model is interesting in so far as it points out to what extent the renormalization of μ is limited : There is a factor $\frac{n_0}{n_0+n_1}$ with the term $\ln\frac{W}{2\hbar\omega_0}$ which is responsible for the renormalization. This means that a good normalisation can take place only when there are enough electrons in the broad part of the band compared to the peak.

VI COHERENCE LENGTH

The rather high peak in the DOS also has another consequence : Louis and al.[9] have measured the critical field Hc_2. The value of ξ (29 Å for K_3C_{60}) they deduce from it is five time smaller than values deduced from calculated Fermi velocity v_f and the BCS formula $\xi = \frac{\hbar v_f}{\pi\Delta}$ (131 Å). We explain this in the framework of our model [10]. The ξ deduced from Hc_2 is an average value over the Fermi surface, which is small owing to the small v_f, high-weight states corresponding to the peak in the DOS. On the other hand, calculated values of v_f usually focus on high-v_f

states. The difference between the two leads to a factor of about 5.

VII CONCLUSION

We have shown that in K_3C_{60} the high value of the DOS, which is responsible for the good value of Tc, is compatible with a sufficient renormalization of the Coulomb repulsion μ (between 1.5 and 2). This is due to the fact that the peak in the DOS has a relatively wide basis and to the contribution of the other bands. This model is also compatible with the variation of Tc upon changing K by another alkaline metal, or upon applying external pressure. The value of the coherence length is also explained in this framework.

This model of a peak in the DOS above a wide band is a general feature of four families of high Tc, short coherence length superconductors: A15, Chevrel phases, cuprates and doped fullerenes [11]. A table of the various values of ξ and v_f is given in ref 11.

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