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NON-LOCAL THEORY OF SUPERCONDUCTING T_c FOR DOPED FULLERENES

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ABSTRACT

The electronic band structures of pure solid C_{60} (fullerene) and the alkali-metal doped solid C_{60} (the superconducting phase) have been calculated using a single-particle, tight-binding Hamiltonian. An accurate and efficient non-local pseudo potential compatible with these bands is employed for the description of the elctron-phonon interaction in the McMillan formula for the superconducting transition temperature T_c. Reasonably good agreement is obtained between our results for some superconducting parameters and the available experimental data.

1. INTRODUCTION

The discovery, by A. F. Hebard et al [1], of superconductivity in alkali-metal-doped C_{60} solid at a relatively high temperature opened up another branch of the field of experimental and theoretical high-T_c superconductivity, which has remained very active ever since. High -T_c superconductivity in doped C_{60} materials is complicated by a number of not-so-well understood features, namely:

i energy multi-band structure, overlap and hybridization,
ii lattice distortions, and
iii coupled electron-lattice motion,

which, in general, lead to obscurity in the microscopic mechanism of this class of superconductors. The afore-mentioned problems complicate the direct application of the existing models of superconductivity such as the BCS [2] and the RVB [3]. It is instructive to digress a little bit in order to indicate the nature of the complications and also to place this work in a proper perspective.

In describing the electron-phonon (el-ph) interaction in conventional metals and superconductors, a central role is played by the assumption of validity of Migdal's theorem [4], which states that vertex corrections in the el-ph interaction can be neglected when the "Migdal parameter" $m = \frac{\omega_c}{E_f}$ is sufficiently small. [Here, ω_c denotes the typical phonon energy and E_f is the fermi energy]. However, unconventional superconductors, such as cuprates and fullerides, are characterized by

fermi entergies E_f much smaller than those of conventional metals. In this situation, the energy scale ω_c can be comparable to E_f so that the quantity ω_c/E_f is no longer negligible as it happens for conventional superconductors, and Migdal's theorem is violated.

Now, Migdal's theorem corresponds to an adiabatic approximation for the dynamics of electrons and phonons and it allows one to neglect vertex corrections and other effects in dealing with the electron-phonon interactions. Within such an approximation it is possible to generalize the BCS theory of superconductivity to include all the many-body effects. This leads to the Eliashberg equations [5-6] for which the most popular expression for T_c is the McMillan one [7]. The contributions of many-body effects within the Migdal-Eliashberg-Mc Millan theory are well known. These many-body effects produce a strong reduction of T_c with respect to the BCS expression and are essential for the conclusion that electron-phonon superconductivity is limited by a maximum $T_c \approx 25k$. This is one of the reasons that has prompted the search for radically new mechanisms for superconductivity in the oxides and fullerides. The breakdown of Migdals' theorem, however, provides us with new approaches to the problem.

Some workers [8-11] believe that one should go beyond Migdal's theorem and include vertex corrections. It is, however, not yet settled whether these corrections will enhance or suppress T_c [see for instance, Ref. 11 for a somewhat full discussion of this issue]. To further complicate matters, Alexandrov and Kabanov [12] have provided a completely different picture by developing a theory of superconducting T_c which takes into account the nonadiabatic effects involving polarons rather than vertex corrections. They then argue that the origin of the breakdown of Migdal's theorem is due to the broken translational symmetry and, any strong enhancement of T_c due to vertex corrections is an artifact of an unrealistic el-ph interaction, whereas the polaronic band narrowing provides such enhancement quite naturally.

In the light of the above unsettled controversies, we have carried out our theoretical analysis in this work within the traditional Migdal-Eliashberg-McMillan framework. In spite of the above controversies, many workers still believe that a BCS type of theory is capable of describing superconductivity in the fullerides [see for instance, Ref. 28]

While studying the structure, symmetry, composition and the energy bands of the pure and the doped C_{60} solid, we arrived at a method of thinking based on an observation that the McMillan's model [7] contains a nonlocal Hamiltonian structure as proposed by Animalu [13]. The non-local term is an extended structure arising from the mutual overlapping or penetration of the wave functions of the constituents of a pair. The pairing is between the S and P wave functions with $\langle \Psi_{s\uparrow} | \Psi_{s\downarrow} \rangle$, $\langle \Psi_{s\uparrow} | \Psi_{p\downarrow} \rangle$ or $\langle \Psi_{s\downarrow} | \Psi_{p\uparrow} \rangle$ and $\langle \Psi_{p\uparrow} | \Psi_{p\downarrow} \rangle$ as the possible probability amplitudes. Technically, the electron-phonon interaction in Animalu's model is

characterized by a non-local pseudo-potential $V_{e\text{-}ph} = (2/3)\varepsilon_f$ where ε_f is the Fermi energy of a particular superconductor. In the case of two electrons forming a Cooper pair, the presence of positive alkali-metal ions can be adjusted via isotopic lifting to make the non-local pseudo-potential sufficiently strong to overcome the usual repulsion between the two electrons in vacuum.

In the section 2 of this work, we discuss the electronic band structures of the pure C_{60} solid and the alkali-metal doped C_{60} solid. The latter band structure has been deduced from our work on the pure C_{60} solid [14]. In section 3 we present a nonlocal theory for some of the relevant superconducting parameters. Discussion of our Results and a conclusion then follow, respectively, in sections 4 and 5.

2. BAND STRUCTURES OF THE PURE AND THE DOPED C_{60} SOLID

The band structure obtained by us for the pure C_{60} solid has been reported already in our preceding paper [14]. N (E), the density of states (DOS), for the t_{iu}^* conduction band was also reported, in addition. The calculation of the DOS was performed with the help of Chadi and Cohen [15] special $\vec{k}$ points and smoothened by convoluting the energy spectrum with a gaussian of width W(E), the band width. The expression

$$w(E) = 0.25eV + 0.5|E - E_{HOMO}| \tag{2.1}$$

where $|E - E_{HOMO}|$ is the energy E measured in eV from the highest occupied molecular orbital (HOMO) level has been adopted by us. The bandwidth and the DOS are then related through the expression

$$w(E) = 2\sqrt{[2\,In\,N(E)]} \tag{2.2}$$

Some theoretical calculations [16, 17] and experiments [18, 19] have revealed that

(i) the band structure of the pure C_{60} solid is not significantly affected by the presence of dopants; the alkali-metal dopants merely transfer their electrons to the t_{iu}^* levels, which are affected only because the lattice constant and consequently the orientation order become modified.

(ii) the distances between the C_{60} molecules in the solid, and consequently the transition Temperature T_c, increase with doping.

These trends are in agreement with a one-electron picture in which the molecular orbitals (MO'S) broaden into bands, and which explains why the value of T_c depends on the crystal structure. As a matter of fact, superconductivity should be linked with the collective effect associated with the structure of the entire sample. T_c can then be accurately described by

$$T_c \propto \frac{\Delta a}{a}$$

or

$$T_c \sim T_o \exp\left(\frac{\Delta a}{a}\right) \tag{2.3}$$

where is the lattice constant of the solid. This is an indication that T_c reflects variation of the bandwidth with pressure (or lattice constant). Experiment [18] has also confirmed that 'a' varies from $14.10\,\overset{o}{A}$ for pure C_{60} solid to $14.50\,\overset{o}{A}$ for Rb_2 Cs-doped C_{60} solid. The band structures for a > $14.10\,\overset{o}{A}$ could then be obtained by allowing the conduction band to scale uniformly with energy and also as a function of lattice constant, as in

$$E_\upsilon^l\left(a\vec{k}\right) \sim \left[exp\left(14.10 - {}^{a}/_{\overset{o}{A}}\right)\right] E_\upsilon^i\left(a\vec{k}\right) \tag{2.4}$$

where $E_\upsilon^l\left(a\vec{k}\right)$ are the electronic energy band structures already calculated [14] for pure C_{60} solid with a = $14.10\,\overset{o}{A}$.

Equation (2.4) has been used to produce the t_{iu}^* band structure for a potassium-doped C_{60} superconducting material (K_3 C_{60}) whose lattice constant is a = $14.25\,\overset{o}{A}$. The band-structure results are plotted in fig. 1 and the Fermi level ε_f is also indicated in the figure. The dispersions are seen to undergo little or no hybridization and remain virtually the same when compared with Fig. 3 of Ref. 14. This is attributed to the experimental findings that the alkali-metal ions play a not-very-critical role in the superconducting system after the donation of their outermost electrons except for structural adjustments where it affects the pressure via the lattice constant or band-width. The calculated bandwidth by us is 0.38 eV which is smaller than the value of 0.447 eV calculated for the pure C_{60} solid.

The corresponding DOS for the doped system is plotted in fig. 2. The calculated DOS at the Fermi level is $N(\varepsilon_f)$ = 15.64 states /mol./eV/spin.

3. NON-LOCAL THEORY OF SUPERCONDUCTING T_C

Since the initial demonstration of T_c = 18k in K_3 C_{60} [1], the superconducting properties of the A_3 C_{60} compounds (A = alkali metal) have been the focus of intense

scrutiny. Significantly less attention has been given to the normal-state properties of these metallic materials. Structural, spectroscopic, and transport measurements have been reported, but several fundamental questions remain to be addressed. Are the alkali-metal doped C_{60} solids fundamentally band like materials as assumed by several explanations of superconductivity in terms of strong electron-phonon coupling λ, or does the small intermolecular overlap lead to correlated carrier motion ?

In the past years several different calculations of the electron-phonon coupling constant λ have been reported for the fullerenes or C_{60} solids. Some of these calculations yield the strongest coupling with the high frequency H_g modes with a moderate electron-phonon coupling, $\lambda \leq 0.5$. On the other hand Picket et al [20] predicted the strongest coupling with the $A_g(2)$ mode and $\lambda \sim 3$. The difference in calculated coupling constants is quite remarkable, and may result in a qualitatively different understanding of the nature of superconductivity of doped fullerenes. Therefore, the experimental determination of λ and more extensive theoretical work are required to clarify these issues. The same comment applies to the traditional coulomb pseudopotential parameter μ^* [see Ref. 21 for a discussion of the controversy on this parameter].

Let us now start with Mc Millan's formula for T_c in the form [7]

$$T_c = \frac{\hbar\omega}{1.2K_B} exp\left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right] \tag{3.1}$$

where the electron-phonon coupling constant is

$$\lambda = N(\varepsilon_f)\ V_{el-ph} \tag{3.2}$$

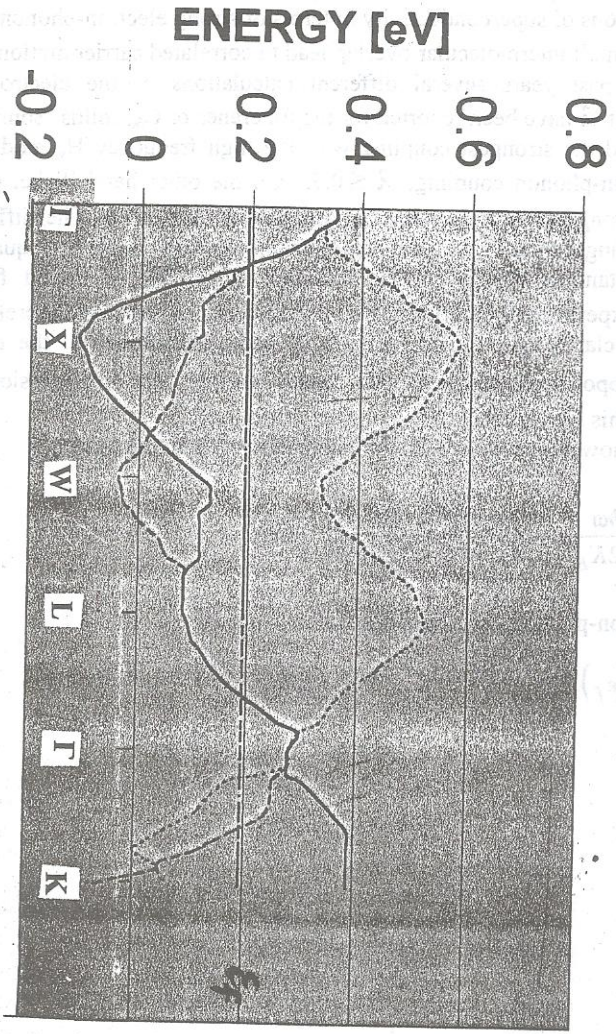

Fig. 1 K_3C_{60} bands;a =14.253A^0.

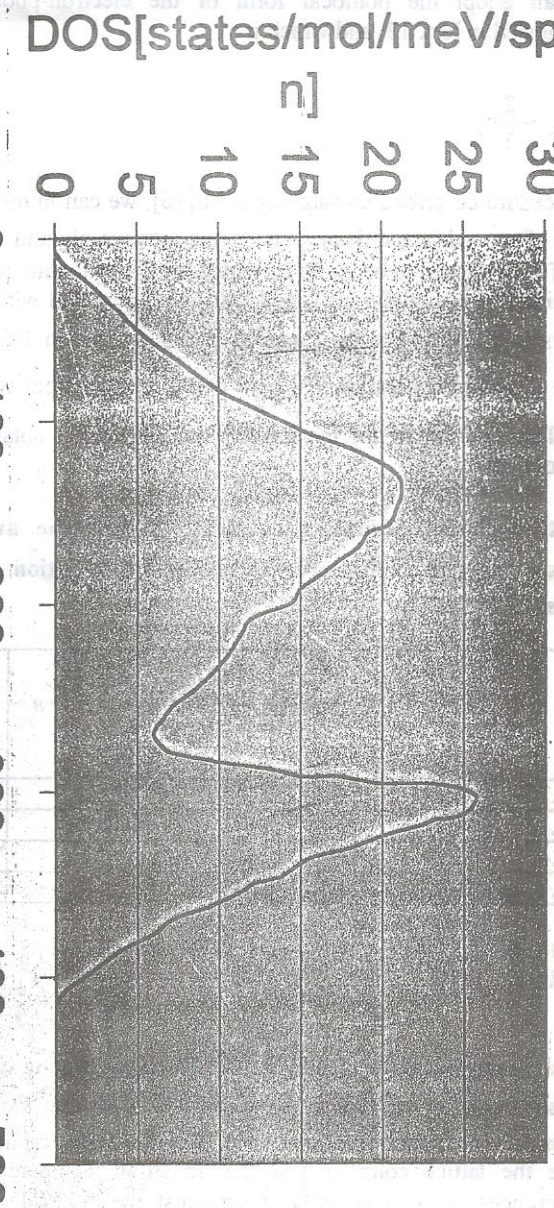

Fig. 7. Density of states of K_3C_{60}.

We shall adopt the nonlocal form of the electron-phonon interaction V_{el-ph}, as suggested in Ref. 13, and which is

$$V_{el-ph} \sim \frac{2}{3}\varepsilon_f \tag{3.3}$$

Following a procedure described by satpathy et al [16], we can immediately evaluate λ as a function of μ^* and hence determine ω (the average phonon frequency) from Equation (3.1) if T_c is chosen to be 20.50 K, which is a typical value for the fullerides. The results obtained in this study and labelled (a) are compared with those obtained by other workers in Table 1. For the range of μ^* considered in Table 1 our results give an average phonon temperature $\hbar\omega/K_B \approx 600$K in agreement with the work of satpathy et al [16]. The reason for the lower value of ≈400k obtained by Tit and Kumar [22] is not clear.

Table 1. Electron-phonon Coupling constant λ and the average phonon frequency ω as a function of the screened coulomb interaction parameter μ^*, with T_c set equal to 20.50k

μ^*	λ a	λ b	λ c	$\hbar\omega/K_B$ (°k) a	$\hbar\omega/K_B$ (°k) b	$\hbar\omega/K_B$ (°k) c
0.15	0.79	0.79	0.98	661	650	403
0.25	1.10	1.11	1.33	612	603	395
0.35	1.47	1.47	1.75	608	604	407
0.45	1.91	1.92	2.25	643	637	438

a present work b LDA-LMTO Results [8]
c LDA Results [12]

Following again the procedure of satpathy et al [16] and employing Equations (3.1) to (3.3) with μ^* set equal to the typical value of 0.2, we show in Table 2 various calculated quantities for the fullerides. The experimental inputs [18] for the calculations are the lattice constant and the transition Temperature T_c. Despite significant differences in ε_f and $N(\varepsilon_f)$ amongst the fullerides, the consistent prediction of 2 as the value of λ is what is particularly significant about Table 2. If

this is found to be experimentally true then this study has provided theoretical verification of Equation (3.1) to (3.3), particularly the nonlocal form of $V_{el\text{-}ph}$ proposed in Ref. 13. In other words, our approach has provided a unified way of looking at the fullerides.

The question whether the rather high value of λ is still consistent with a Migdal-Eliashberg-McMillan theoretical framework is outside the scope of this study. Further work is definitely required, even if it is not on this difficult question. For instance, it would be nice to modify the theory sketched in this work a little bit so as to have the results of the average phonon frequency in Table 1 consistent with those in Table 2. Though such an inconsistency was also pointed out in the work of Tit and Kumar [22], this issue is currently been addressed.

Table 2: Calculated Superconducting Parameters, with the lattice constant a and the transition Temperature T_c taken as Experimental inputs.

	A_3C_{60}				
A_3	K_3	K_2Rb	Rb_2K	Rb_3	Rb_2Cs
T_c(K) §	19.28	21.80	26.40	29.40	31.30
a (Å) §	14.253	14.299	14.364	14.436	14.493
d(Å) ¶	3.128	3.161	3.207	3.258	3.298
$N(\varepsilon_f)$ [states/mol./eV] ¶	15.64	16.38	17.48	18.78	19.88
$N(\varepsilon_f)$ [states/mol./eV] $	17.17	18.02	18.42	18.93	19.33
ε_f (eV) ¶	0.192	0.183	0.172	0.160	0.151
λ ¶	2.000	1.998	1.992	1.990	2.000
$\hbar\omega / k$ (K) ¶	173	195	237	264	280
$\left\lvert \frac{d\ln V_{e-ph}}{d\ln N(\varepsilon_f)} \right\rvert$ ¶	1.22	1.22	1.32	1.42	1.48

§ experiment[18]
¶ present work
$ LDA results [22]

4 RESULTS AND DISCUSSION

Estimated values of $N(\varepsilon_f)$ in the present work ranged between 15.0 and 20.0 states/mol./eV./spin. These values lie between those reported from susceptibility measurements [19]. However, the values of $N(\varepsilon_f)$ are generally uncertain; magnetization measurements [19] predicted values in the range 10 to 15 states/mol./eV./spin while the extended Huckel data [23] predicted $N(\varepsilon_f) \geq$ 20states/mol./eV./spin . Some LDA calculation [23,24] yield values between 6.6 and 12.5states/mol./eV./spin for K_3C_{60} superconducting material. The values of ε_f calculated by us (row8 of table 2) ranged between 0.15 and 0.20eV. Our estimated

value of ε_f for K_3C_{60} is 0.192eV while Xu et al [25] reported 0.18eV in an LDA calculation.

Different values of the electron-phonon coupling constant (λ) have been reported. Some calculations [17,26] gave $\lambda \leq 0.5$ while Picket et al [20] predicted $\lambda \cong 3$. Estimated value of λ in the present work is approximately 2.0; this agrees with the suggestion [12] that superconductivity in alkali-metal doped fullerene be a non-adiabatic phenomenon in which λ is necessarily strong i. e. $\lambda \geq 1$ to overcome the Coulomb repulsion.

The unified model results presented here is consistent with an increase in T_c as separation between fullerenes increases due to the selection of the alkali-metal dopant. Increasing the separation between fullerenes does not reduce the intrinsic electron-phonon coupling since one is concerned here with the modulation of the overlap matrix element for two neighbouring atoms in a fullerene. Nevertheless, $V_{e\text{-}ph}$ is slightly reduced due to slight reduction in k_f. On the oher hand, the electronic density of states increases due to the narrowing of bands which comes about as a result of decrease in coupling between fullerenes.

The quantity $|d \ln V_{e\text{-}ph}/d \ln N(\varepsilon_f)|$ calculated by us (last row of table 2) is expected to be less than 1. Although these values are still on the high side, they are better than those reported in [22]. The value of this quantity improves with an increase in μ^*. However, allowing the Coulomb repulsion energies to be close to conduction bandwidth (~ 0.5eV) will put A_3C_{60} superconductors in a dicey region (of becoming an insulator again). The values of d (intermolecular distance) calculated here are very reasonable. They are in good agreement with the result of other workers [27].

The average phonon frequencies ω calculated here (9th row of table 2) range between 170 and 300K. These values appear too low, but they are reliable based on the assumption that the phonons involved in the pairing mechanism of the alkali-metal doped C_{60} be the lower-frequency intramolecular modes with large λ.

5 CONCLUSION.

An investigation of the band structure of doped C_{60} solid has been carried out. Special attention was given to t^*_{1u} – being the LUMO that is partly occupied in the alkali-metal doped C_{60} (superconductors). The sub-band dispersion, described in section 2 is shown in Fig. 1 while the density of states calculated for the t^*_{1u} MO's is plotted in Fig. 2

The insight gained from the band structure led to further investigations on the effects of alkali-metal doping and the associated lattice constant change. We adopt specially, the unified (non-local pseudo-potential) model which allowed the superconducting parameters to be estimated as functions of the lattice constant.

Our approach is very useful in revealing the patterns of electronic structures, band energies, band-widths and density of states as the system evolves from the normal to the superconducting state as well as making contact with other models in current literature.

Finally, our results are in favour of electron-phonon pairing mechanism; this is seen in our density of states which increases with ion mass.

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