

The effect of ammonia intercalation on the superconducting properties of the alkali-metal doped fulleride

F. Matthew-Ojelabi
Department of Physics,
University of Ado-Ekiti, Ado-Ekiti, Nigeria, Nigeria

Abstract

A theoretical investigation of the electronic properties of the relatively high- T_c alkali-metal doped superconducting fullerides when they are further exposed to ammonia molecules as dopants is presented. Our numerical method relies on a group theoretical technique for the formation of molecular orbitals (MO's) for the solid C_{60} using 60 radial atomic orbitals (AO's) derived in a previous work. We also take into consideration the fact that the Fermi energies of the fullerides compare favourably with their phonon energies in the choice of a T_c formula. The effect of the ammonia molecules, as intercalants, on the density of states at the Fermi level ($N(\epsilon_f)$) and consequently superconductivity are then discussed

1.0 Introduction

The electronic states and properties of superconducting alkali-metal-doped C_{60} (fullerides) with stoichiometric composition A_3C_{60} where $A_3 = K_3, K_2Rb, Rb_2K, Rb_3$ and Rb_2Cs have been studied extensively by various experimental and theoretical techniques (cf. Jost *et al* (1991) [3], Hebard (1992) [1], Satpathy *et al* (1992) [11], Nacir and Kumar (1993) [7], Laouini *et al* (1995) [4], Matthew-Ojelabi (2004) [6]. However, very little is currently known of the analogous properties for the ammonia-intercalated superconducting C_{60} material $(B_3)_x A_3 C_{60}$ with $B_3 = NH_3$ and $x > 1$).

Ammonia molecules as intercalants in the interstices of A_3C_{60} compounds are meant to induce further expansion that will stimulate further changes in lattice parameter and thus the unit cell volume (Ricco *et al* (2000, 2001, 2003 and 2005, [8], [9], [10])). In view of this, the t_{1u} conduction band of A_3C_{60} compound narrows down and the density of states at the Fermi energy level ($N(\epsilon_f)$) increases with attendant boost in the T_c 's of the ammonia-doped A_3C_{60} superconductors.

A regular increase observed in T_c as function of cation radius or lattice parameter in fullerides is a well-known Eliashberg theory. Behind this theory is a notion that the phonon-mediated pairing mechanism is wholly responsible for superconductivity. This scenario suggests a T_c that strongly depends on the density of states (DOS) at the Fermi level ($N(\epsilon_f)$) - a quantity which naturally increases with band narrowing caused by lattice expansion. The resounding success recorded through this approach necessitates the search for further expansion of the lattice parameter by other particles that will not tinker with the composition and therefore the superconductivity of these fullerides. There is no doubt that the neutral ammonia molecules rightly fit into this picture. Within the ammonia intercalated superconductors, $(NH_3)_x$ -A group occupies large octahedral (O) sites of the face centre cubic (fcc) lattice and breaks the cubic symmetry of the crystal field. This causes a lift of the degeneracy of the $C_{60} t_{1u}$ lowest unoccupied molecular orbitals (LUMO'S) and thus induces a bandwidth decrease and a corresponding increase in $N(\epsilon_f)$ as well as T_c .

While this scenario holds for certain ammonia-doped A_3C_{60} superconductor e.g. $(NH_3)_4Na_2CsC_{60}$ whose T_c increases from 10.5K to 29.6K, the reverse is the case for $(NH_3)_xNaK_2C_{60}$ and $(NH_3)_xNaRb_2C_{60}$, which both become insulating and anti-ferromagnetic after further exposure to ammonia molecules. However, it is possible to restore superconductivity by applying external pressure to the bulk. Beside this trend, other anomalous features are known to exist.

The determination of the basic superconducting properties requires detailed knowledge of the electronic structure for the pure as well as the doped materials. This is fundamental since the phenomenon of superconductivity embodies the collective effect associated with the structure of an entire sample. The knowledge of bandwidth leads to that of DOS at the Fermi level for each sample and consequently T_c .

This paper aims at investigating the superconducting nature of the ammonia-alkali-metal-doped C_{60} fullerides ($(NH_3)_x-A_3C_{60}$) theoretically using the Schluter *et al* (1992) [12] estimate for V_{e-ph} in the T_c formula of Zheng and Beneman (1992) [13]. This becomes necessary due to the inadequacy of the McMillan formula to fully account for superconductivity in the ammonia-doped A_3C_{60} superconductors. Our approach is based on the electronic structure calculation of an earlier work (Matthew-Ojelabi and Idiodi (2001) [5], Matthew-Ojelabi (2004) [6]) by means of a Bloch vector-dependent single-particle tight-binding Hamiltonian and t_{lu} LUMO's (lowest unoccupied molecular orbitals).

In the remaining part of this paper, we shall outline briefly in section 2, the important expressions needed while the preceding section summarizes the calculation procedures. Also, we shall present estimated values for superconducting parameters of some fullerides using the Zheng-Benemann (1992) [13] formulation in section 4 before conclusion.

2.0 Theory

The pressure-dependence of T_c for the fullerides has been studied extensively. It is well-known that increasing the pressure on a sample reduces the lattice spacing and consequently T_c . Thus, the knowledge of compressibility enables us to convert pressure-dependence to a dependence on lattice parameter and being able to apply pressure to reduce the lattice parameter within certain fullerides (to obtain higher T_c) indicates that it is the electronic overlap between orbitals that is responsible for superconductivity. Experimentally, T_c has been described by

$$(2.1)$$

$$T_c \sim T_0 \exp\left(\frac{\Delta a}{a}\right)$$

where $\Delta a/a$ represents the fractional lattice parameter change. T_c , as observed in equation (2.1), reflects the variation of bandwidth with pressure while the coupling constant (λ) remains fixed.

In theory and as a rule, the Eliashberg equations are solved assuming a two-peak distribution function for the phonon modes. If $\epsilon_f \gg \omega_{ph}$ where ω_{ph} is the characteristic phonon energy and ϵ_f the Fermi energy then the result is a well-known Migdal-Eliashberg formulation re-packaged as McMillan T_c formula given by

$$T_c = \frac{\hbar\omega}{1.2k} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right) \quad (2.2)$$

The coupling constant is related to DOS at Fermi level $N(\epsilon_f)$ through

$$\lambda = N(\epsilon_f)V_{e-ph} \quad (2.3)$$

where the coupling matrix V_{e-ph} measures the strength of the interaction between electrons and excitations (phonons). Equation (2.2) is valid for $\lambda \leq 1.5$ and $N(\epsilon_f)V_{e-ph} \gg \mu^*$ (electron-electron repulsion).

However, in doped fullerenes (fullerides) it is imperative to use a better prescription by directly solving the Eliashberg equations since $\epsilon_f \sim \omega_{ph}$ (on-molecule phonon energies). By using the linearized form of the Eliashberg equations one obtains a T_c expression of form (Zheng and Benemann (1992) [13])

$$T_c = 1.134\epsilon'_f \exp\left(\frac{-Z_1(0) + \lambda \langle \ln[\epsilon'_f + \Omega/\Omega] \rangle}{\lambda - \mu - \delta}\right) \quad (2.4)$$

Quantity $Z_1(0)$ represents a renormalization function describing phonon dressing of electrons at the Fermi surface which, as a matter of fact, should be a function of the phonon frequency Ω as indicated by

$$Z_1(0) = 1 + \lambda - \int_0^{\infty} \frac{2d\Omega}{2\varepsilon_f} \sum_k \frac{B_k(\Omega)gk^2}{\Omega} - \frac{\Omega}{\varepsilon_f + \Omega} \quad (2.5)$$

In our calculation we shall employ equation (2.5) instead of $Z_1(0) = 1 + \lambda$ for ordinary metals usually used in equation (2.2). $Z_1(0)$ strongly depends on the phonon density of states of the k^{th} phonon branch symbolized by $B_k(\Omega)$ and on g_k the corresponding electron-phonon coupling constant. It should be mentioned that smaller values of $Z_1(0)$ favour higher T_c as indicated by $T_c \propto \exp[-Z_1(0)/\lambda]$. The renormalized half-bandwidth ε'_f (i.e. renormalized Fermi energy) is an increasing function of phonon frequencies since renormalization comes from the retardation of electron-phonon interaction. In addition, $Z_1(0) < Z(0)$ and $Z_1(0) \rightarrow Z(0)$ as $\varepsilon'_f \rightarrow \infty$. Parameter μ represents the dimensionless Coulomb repulsion for the low-lying electronic excitations and δ , by all means, should be small (< 0.01) and the fact that equation (2.4) reduces to equation (2.2) if $\varepsilon'_f/\Omega \gg 1$.

The intermolecular AO hopping integrals decay rapidly with the inter-molecular distance d and are expressed in terms of the two-centre atomic integrals $V_{ss\sigma}(d)$, $V_{sp\sigma}(d)$, $V_{pp\sigma}(d)$, and $V_{pp\pi}(d)$ specified by

$$\langle n'|H|n \rangle = -[V_{\sigma}(d) - V_{\pi}(d)](\mathbf{R}_{n'} \cdot \mathbf{d})(\mathbf{R}_n \cdot \mathbf{d}) + V_{\pi}(d)(\mathbf{R}_{n'} \cdot \mathbf{R}_n) \quad (2.6)$$

where \mathbf{R}_n is a unit vector in the direction of p-orbital on an atom n (radial direction). Also, $\hat{\mathbf{d}}(=\mathbf{d}/d)$ is a unit vector in the direction of atom n' to atom n . However, $V_{ss\sigma} = V_{sp\sigma} = V_{pp\sigma} = V_{\sigma}$ and $V_{pp\pi} = V_{\pi}$. The distance dependence of the hopping integrals between carbon atoms on neighbouring molecules is an exponential decay written as

$$V_{\sigma}(d) = V_{\pi}(d) = (d/d_0) V_0 \exp[-(d - d_0)/L] \quad (2.7)$$

We shall account for the variation of lattice parameter by modifying the hopping integrals via a change within the intermolecular distance. Thus Eq.(7) scales according to

$$V_{\sigma}(d) = V(a) = (d(a)/d) V \exp[-(d(a) - d)/L] \quad (2.88)$$

where $d(a)$ is the nearest neighbour distance for different contacts. Quantity d is the molecular distance at $a = 14.10\text{\AA}$. Thus, $d(a)$ concurs with

$$d(a) = (a/\sqrt{2}) - 6.95\text{\AA} \quad (2.9)$$

Parameter L is usually fitted to the experimental value (0.505\AA) of Fleming *et al.* or the LDA value (0.58\AA) (cf. Nacir and Kumar (1993)). The band structures for $a > 14.10\text{\AA}$ are determined by scaling the conduction band uniformly with energy and as a function of the lattice parameter in line with

$$E_j(a, ak) \sim [\exp(14.10 - a/\text{\AA})] E_j(ak) \quad (2.10)$$

$E_j(ak)$ represents the energy band structures calculated with $a = 14.10\text{\AA}$ using t_{1u}^* MO's.

The band structures of solid C_{60} are little affected by the presence of alkali-metal atoms or (and) ammonia molecules as dopants. The extra particles enter the t_{1u}^* band which is only affected by the fact that the dopants simply modify the lattice parameter and to a little extent the orientation.

3.0 Calculation procedure

As a first step, the band structures for the fullerides and ammonia intercalated fullerides are calculated by means of Eq.(10). Technically, the averaged phonon frequency ω_{ph} , the electron-phonon interaction V_{e-ph} and the screened Coulomb interaction μ are independent of the intermolecular separation $d(a)$. We shall obtain the d -dependence of $N(\varepsilon_f)$ from our band structure calculations.

Based on the knowledge that the electrons couple strongly to the lower-frequency buckling modes with frequencies in the range $300-800\text{ cm}^{-1}$ and to the higher-frequency tangential modes in the range $1400-1600\text{ cm}^{-1}$, we shall set (in the manner of Schluter *et al* (1992) [12]).

$$\lambda = [1/(2\varepsilon_f)] \sum_k 2g_k^2 / \Omega_k = [\tau/(2\varepsilon_f)] \sum_k V_k \quad (3.1)$$

where τ is a proportionality constant. The renormalized Fermi energy can be obtained through

$$Z_1(\varepsilon_f) \varepsilon_f = \varepsilon_f \quad (3.2)$$

Meanwhile, the dependence of λ on $d(a)$ enters through $N(\varepsilon_f)$ which we shall parameterize as

$$N(\varepsilon_f) = B/W^{t_{1u}^*} \quad (3.3)$$

where B is an arbitrary constant. The bandwidth is also parameterized as (having set $L=0.58\text{\AA}$)

$$W \sim d(a) \exp[-d(a)/0.58\text{\AA}] \quad (3.4)$$

$$N(\varepsilon_f) \sim B/\{d(a) \exp[-d(a)/0.58\text{\AA}]\} \quad (3.5)$$

$$\lambda = [B/d(a)] \exp[-d(a)/0.58\text{\AA}] V_{e-ph} \quad (3.6)$$

$$\ln \lambda = \ln B + \ln V_{e-ph} - \ln d - (d/0.58\text{\AA}) \text{ , } V_{e-ph} \text{ is constant} \quad (3.7)$$

This implies that
$$\frac{d\lambda}{\lambda} = -\frac{dd}{d} - \frac{1}{0.58\text{\AA}} \quad (3.8)$$

The dimensionless Coulomb repulsion μ is important since there must be scattering into higher lying states. This situation causes electronic hop within C_{60} molecules at a much faster rate than that caused by ε_f . Instead of bare Coulomb repulsion μ , we shall use the reduced form given by (Schluter *et al* (1992) [12])

$$\mu' = \mu/[1 + \mu \ln(\omega_{el}/\omega_{ph})] \quad (3.9)$$

Here, ω_{el} is the overall Coulomb scattering energy scale and the phonon frequency $\omega_{ph} \sim \varepsilon_f$. We have kept all on-molecule parameters constant and assume a d -dependence for ε_f of form

$$(\varepsilon_f'/\varepsilon_f) = (d/d')^n \quad (3.10)$$

Here, $d' = d(a)$ (the intermolecular distances in fullerenes) and d gives the intermolecular distances in the pure solid C_{60} .

4.0 Results and discussion

The band structure calculated analytically with t_{1u}^* MO's (lowest unoccupied molecular orbitals (LUMO's)) for pure solid C_{60} with $a=14.10\text{\AA}$ of present work was displayed in Figure 1. The t_{1u}^* MO's are relevant to superconductivity. From our calculation, the size of the bandwidth W , is $\sim 447\text{meV}$. Without loss of Physics, we assumed a square shape with smoothing by a Gaussian for the density of states (DOS) and set

$$N(E) = \begin{cases} (2\varepsilon_f)^{-1}, & \text{for } E \leq \varepsilon_f \\ 0, & \text{otherwise} \end{cases} \quad (4.1)$$

Here, $W = 2\varepsilon_f$ having assumed that the band was half-filled. The results were plotted in Figure 2. We also use the group theoretical values of $d(=3.04\text{\AA}$ for pure solid $C_{60})$ and its lattice parameter-dependence (Equation (2.9)) to obtain d' for the fullerenes (see column 3 of Table 1). To evaluate T_c and other superconducting parameters through equation (2.4) and equation (3.10), we used the estimate of Zheng and Benemann (1992) [13] for $Z_1(\omega)$ (see Figure 3) and the experimental values of a . The results were listed on the table below. From the table, it was observed that the calculated results compared favourably well with experiment where available. Further observation of the fullerenes on the table (especially rows 7 and 8) showed that the process of additional doping with ammonia molecule actually increased the lattice parameter and hence the T_c .

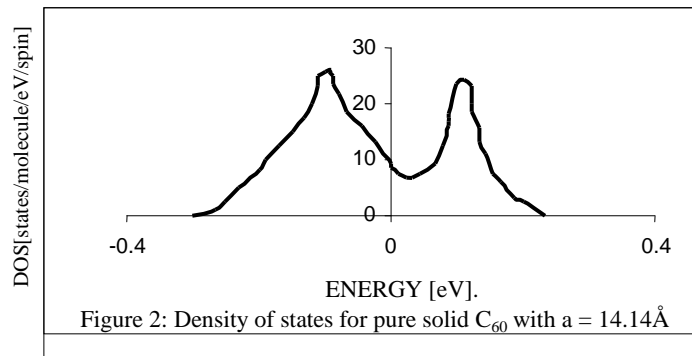
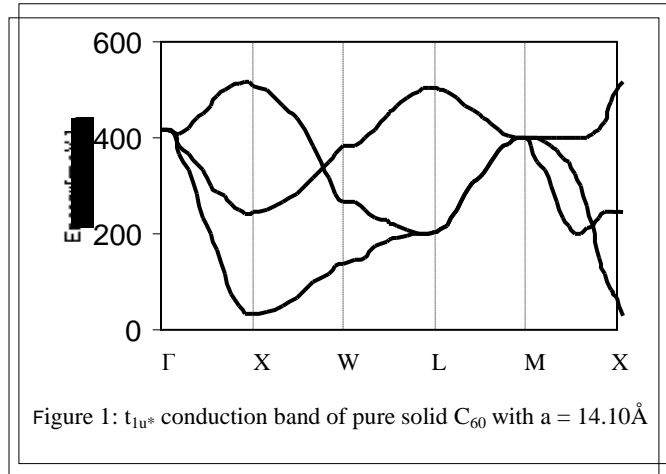
Table1: Superconducting parameters of certain fullerenes

Fulleride	$T_c(\text{K})$ (a)	$d'(\text{\AA})$ (a)	$d(\text{\AA})$ (b)	$a(\text{\AA})$ (a)	$a(\text{\AA})$ (b)	$N(\varepsilon_f)$ States/mol./eV. (b)	$\varepsilon_f'(\text{eV})$ (b)
K_3C_{60}	19.28	3.128	3.152	14.253	14.286	15.64	0.192
K_2RbC_{60}	21.80	3.161	3.194	14.299	14.346	16.38	0.183
Rb_2KC_{60}	26.40	3.207	3.260	14.364	14.440	17.48	0.172
Rb_3C_{60}	29.40	3.258	3.298	14.436	14.493	18.78	0.160
Rb_2CsC_{60}	31.30	3.298	3.319	14.493	14.523	19.88	0.151

$\text{Na}_2\text{CsC}_{60}$	10.5	-	2.942	-	13.989	13.88	0.208
$(\text{NH}_3)_4\text{Na}_2\text{CsC}_{60}$	29.60	-	3.300	-	14.496	17.49	0.173
$(\text{NH}_3)_{0.75}\text{NaK}_2\text{C}_{60}$	11.80	-	2.982	14.36	14.046	12.76	0.219
$(\text{NH}_3)_{0.85}\text{NaK}_2\text{C}_{60}$	9.00	-	2.888	14.38	13.914	14.86	0.198
$(\text{NH}_3)_{1.6}\text{NaRb}_2\text{C}_{60}$	25	-	3.242	-	14.413	17.24	0.175

a: Experimental results of Ref.[2, 8]

b: theoretical results of present work



5.0 Conclusion

We have demonstrated theoretically in this work that superconductivity in fullerides can be improved by further reducing the band gap by inserting neutral molecules – say ammonia molecules. Fundamental questions remain to be answered on why the non-conventional BCS nature of some superconducting condensates. The non-conventional behaviour is clearly evident in the superconducting phase of $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$ where progressive increase in ammonia concentration of $\text{NaK}_2\text{C}_{60}$ produces an increase in lattice parameter but an unexpected decrease in T_c .

References

- [1] F. Hebard "Superconductivity in doped fullerenes" *Phys. Today*, vol. 45, pp. 26-32, 1992.
- [2] R. M. Fleming *et al* "Clusters and cluster-assembled materials", ed. by R. S. Averback *et al*, *MRS Symposia Proceedings (Mats. Research Soc., Pittsburgh)* vol. 206, pp. 691-701, 1991.
- [3] M. B. Jost, N. Troullier, D. M. Poirier, J. L. Martins, J. H. Weaver, L. P. F. Chibante and R. E. Smalley, "Band dispersion and empty electronic states in solid C_{60} : Inverse photo-emission and theory", *Phys Rev. B*, vol. 44, pp. 1966-1971, 1991.
- [4] N. Laouini, O. K. Andersen and O. Gunnarson, "Analytical molecular orbitals and band structures of solid C_{60} ", *Phys. Rev. B*, vol. 51, № 24, pp. 17446-17478, 1995.
- [5] F. Matthew-Ojelabi and J. O. A. Idiodi "Group theoretical foundation for the molecular orbitals of the solid C_{60} ", *J. Nig. Ass. Math. Phys.*, vol. 5, pp. 201-220, 2001.
- [6] F. Matthew-Ojelabi, "The theory of high- T_c superconductivity in an alkali-metal doped organic material", *Advances in modeling and analysis, C*, vol. 65, no.1, pp. 77-86, 2004.
- [7] Tit Nacir and Vijay Kumar, "Empirical tight-binding parameters for solid C_{60} ", *J. Phys. Condes. Matter*, vol. 5, pp. 8255-8264, 1993.
- [8] M. Ricco, T. Shiroka, A. Sartori, F. Bolzoni and M. Tomaselli "Electronic properties of $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$ ", *Europhys. Lett.*, vol. 53, № 6, pp. 762-768, 2001.
- [9] M. Ricco, G. Fumera, T. Shiroka, O. Ligabue, C. Bucci and F. Bolzoni, "Metal-to insulator evolution in $(\text{NH}_3)_x\text{NaK}_2\text{C}_{60}$: an NMR study", *Phys. Rev. B*, vol. 68, № 1, pp. 0351021-0351026, 2003.
- [10] M. Ricco, T. Shiroka, M. Belli, D. Pontiroli and M. Pongliari, "Unusual polymerization in Li_4C_{60} fulleride", *Phys. Rev. B*, vol. 72, № 1, pp. 155437-155442, 2005.
- [11] Satpathy, V. P. Antropov, O. Jepsen, O. Gunnarson and A.I. Liechtenstein "Conduction band structure of alkali-metal doped C_{60} ", *Phys. Rev. B*, vol. 46, № 3, pp. 1773-1793, 1992.
- [12] M. Schlüter, M. Lannoo, M. Needels and G. Baraff "Electron-phonon coupling and superconductivity in alkali-metal intercalated C_{60} solid", *Phys. Rev. Lett.*, vol.68, № 4, pp. 526-529, 1992.
- [13] H. Zheng and K.H. Bennemann, "Calculation of the superconducting critical temperature in doped fullerenes", *Phys. Rev. B*, vol. 46, № 19, pp. 11993-12000, 1992.