

Electron-phonon Pairing Mechanism for Superconductivity in K_3C_{60} Fullerides

Daluram Yadav, Nishchhal Yadav, Sanjay K. Ghosh*

School of Studies in Physics, Vikram University, Ujjain, India

*Corresponding author: daluramyadav@gmail.com

Received December 28, 2012; Revised February 02, 2013; Accepted February 28, 2013

Abstract The electron pairing mechanism leading to superconducting state in K_3C_{60} fullerenes is explored within the framework of strong coupling theory. The intermolecular interactions between C_{60} cages and expansion of lattice due to the intercalation of K atoms are investigated using the nearest neighbor interactions. The renormalized Coulomb repulsive parameter μ^* and the electron phonon coupling strength λ are obtained for the intermolecular phonon frequency ω_{er} , keeping in mind that the free electrons in lowest molecular orbital are coupled with intermolecular phonons. T_c is then estimated as 5 K, which is much lower as compared with the reported value. The electrons also couple with the intramolecular phonons then T_c enhances to 22 K. In this approach the carbon isotope effect exponent, the energy gap ratio, effect of pressure and volume on T_c is calculated which support the superconducting state.

Keywords: fullerenes, intermolecular phonons, intramolecular phonons, transition temperature, carbon isotope effect, energy gap ratio

1. Introduction

Superconductivity in alkali metal intercalated Buckminster fullerenes with medium superconducting transition temperature ($T_c \sim 20$ to 45K) [1] continue to provoke considerable interest. The attractive pairing mechanism with conventional phonon mediated electron pairing mechanisms in superconducting fullerides is a central point of several experimental studies. The normal state electronic and magnetic properties of alkali metal intercalated fullerides are still only partially understood and are reviewed at great length [2]. Superconductivity in light-element materials entered in a new era after the recent observation of a critical temperature as high as 38K in Cs_3C_{60} [3] and the birth of a new family of organic superconductors based on aromatic molecules, as doped picene [4], phenanthrene [5], coronene [6] and dibenzopentacene [7]. The unavoidable question about the “pairing glue” in the fullerides seems to have an answer at least for the standard members of the family, like K_3C_{60} or Rb_3C_{60} . For these compounds there is convincing evidence of an electron - phonon driven superconductivity, in which Jahn-Teller coupled intramolecular vibrations play the main role [8]. Nonetheless, the anomalous properties of “expanded” fullerides with large intermolecular distance, like ammoniated compounds [9] and most notably Cs_3C_{60} suggest that labeling these materials as standard superconductors described by the Bardeen-Cooper-Schrieffer (BCS) theory is at least hazardous. This compound is synthesized in two different crystal structures, the fcc which is common to most doped fullerides and a A15 structure, with a bipartite lattice [10].

A - 15 Cs_3C_{60} at ambient pressure is an anti ferromagnetic insulator with $T_N = 46$ K and a spin-1/2 moment at each molecule [11], as opposed to K_3C_{60} and Rb_3C_{60} , which are superconductors in the same conditions.

The doping in C_{60} as A_3C_{60} ($A = K, Rb, Cs$) are at the centre of many novel phenomenon points to their technological and industrial importance. Neutron inelastic scattering measurements [12] and Raman spectroscopy [13] have been extensively used to probe the molecular vibration modes of C_{60} in pristine and doped C_{60} solids, to investigate aspects related to structural and electron-phonon interaction in superconducting fullerides. Neutron scattering [12] indicated that the vibration spectrum of K_3C_{60} may be divided into two regions, one of them belongs to the rotation of C_{60} molecule and the intermolecular vibrations in the range of 2.5 to 25meV and the others are the intramolecular mode with frequency 25 to 200meV. Raman scattering [13] yields the on-ball vibration modes (~ 40 meV - 0.2eV). In passing we note that, the phonon spectrum in AMIF consists of mode of C_{60} ($26cm^{-1}$), the vibrations of K^+ ions and the translational vibrations as a whole ($\sim 45cm^{-1}$ - $120cm^{-1}$) and the on ball molecule vibrations ($\sim 260cm^{-1}$ - $1900cm^{-1}$) as revealed from lattice dynamic studies [14].

The carbon isotope effect $\alpha_C = 0.30 \pm 0.05$ with the 100 % substitution of ^{13}C for ^{12}C [15] naturally favours the phonon mediated pairing. In the report of Fuhrer and coworkers, a reduced α , of about 0.21 \pm 0.012 is documented [16]. We note that the Rb dopant isotope effect measurements verify that intermolecular phonons do not play a significant role in AMIF [17]. Later on, Burk and coworkers [18] have shown a rubidium isotope effect of $\alpha_{Rb} = -0.028 \pm 0.036$, a result which implies that the alkali- C_{60} optic phonons play at most a minor role in the

pairing mechanism. However, a substantial intercalated isotope effect is expected in a situation with significant contribution from alkali- C_{60} optic phonons. We note that the value of αRB may hint at a similarity with the inverse hydrogen isotope effect in strongly anharmonic palladium hydride [19].

It is generally believed that the AMIF holds wave symmetry of the order parameter [20]. Tunneling measurements predicts a large energy gap ratio ($\beta = 2\Delta_0/kBT_c$) of 5.3 ± 0.2 for K_3C_{60} led to strong coupling regime [21]. Although tunneling measurements predicts a large magnitude of the reduced energy gap then the BCS theory ($\beta = 3.53$) support a low energy intermolecular phonons as the source of superconductivity. However, several other reports on energy gap i.e., infrared spectroscopy [22], muon spin relaxation measurement (μSR) [23] and absolute reflectivity data [24] provides energy gap value of $3.6 \sim 4.0$ close to the BCS weak coupling limit favors the intermolecular phonons. These values are also near those obtained from nuclear spin relaxation measurement [25]. Optical and tunneling studies [26] on Rb_3C_{60} led to $\beta = 4.2$ indicate that the superconductivity cannot be described in the weak coupling limit. Zhang and coworkers [27] first proposed that the doped alkali ion phonon mode produce a strong attraction for electrons on C_{60} using a Hubbard model to describe the superconductivity. In the theory of Varma et al. [28] the electron-phonon interaction in fullerides is induced by high frequency intramolecular vibration modes on a ball of C_{60} and it should be a key feature of superconductivity. The electron-phonon coupling parameter (λ_{ra}) is evaluated as 0.11.

The same follows from Schluter et al. [29]. The accurate results reflected from the self-consistent approach for intramolecular vibration [30]. However, the theory of Zhang and Guo led to the fact that the coupled K^+ optical mode and the vibration of C_{60} mass centre will induce a strong electron-phonon interaction [31]. They have pointed that the value of electron-phonon coupling parameter for the intermolecular vibrations is too small to explain the superconductivity. Ivanov and Maruyama [32] have proposed a three square well model which is characterized by windows of low-frequency intermolecular phonons, high- frequency intramolecular and Coulomb energy and find that these interactions allows a coherent interpretation of superconducting fullerides properties. Furthermore, Alexandrov and Kabanov [33] have developed a non-adiabatic theory of super- conductivity.

The transition temperature T_c monotonically changes with lattice constant a . The value of a can be changed or by pressure or by substitution of different ions instead of starting. The pressure effect in fullerides is huge, dT_c/dP is negative, $dT_c/d\ln a$ for different fullerides are close to each other. The direct measurements of the pressure dependence of the superconducting T_c for K_3C_{60} by Sparr and coworkers [34] noticed that T_c ($= 19.3$ K), decreases strongly with increasing pressure, $dT_c/dP = -7.8$ K/GPa. Subsequently, measuring magnetic susceptibility [35] under hydrostatic pressure yields $dT_c/dP = -9.7$ K/GPa with a T_c of 29.6 K for single-phase Rb_3C_{60} . In the theory of Chaban, the dependence of T_c on the pressure is argued

to be connected with the chemical pressure effect in fullerides [36].

It is widely believed that the high frequency ($\sim 400 - 1400$ cm^{-1}) intramolecular modes or electronic excitation would tend to favour the strong coupling theory while intermolecular modes (~ 150 cm^{-1}) would require normally weak coupling theory. In the fullerenes K_3C_{60} , the intermolecular vibrations possess the energy in the range 2.5 to 25meV and the band structure calculations [37] have reported Fermi energy (ϵ_F) as 0.2 - 0.3eV. Looking to the various experimental reports [1,2 and 12-26, 34-37] and theoretical proposals [27-33], we have made our efforts to reveal the nature of pairing mechanism and physical properties leading to superconducting state, by considering the three dimensional K_3C_{60} as a diatomic lattice with C_{60} molecule and alkali metal (K) ions.

2. Methodology

The undoped C_{60} molecule is a pure carbon compounds and possesses a spherical structure. The nuclear cage of C_{60} have a diameter of 7.1 Å with 2 bond length (6-6 ring) 1.4 Å and (6-5 ring) 1.46 Å. The distance of the nearest approach in the molecular solid is 3.1 Å [38]. The C_{60} molecule crystallizes in the fcc phase with lattice parameter $a = 14.20$ Å and the distance between the centers of the nearest neighbour C_{60} cages is $b = a/\sqrt{2}$. Furthermore, in C_{60} molecule, out of 4 valence electrons on each carbon atom, 3 electrons participate in the 90 σ bonds along the edges of truncated isocahedron and the remaining 60 electrons of the molecule are in the orbital. In fact, the diameter of C_{60} molecule is large in such a way that the electron density is localized near the, surface of the sphere. Electronic energy band structure [39] reveals that for C_{60} , the lowest unoccupied molecular orbital is empty and can accommodate 6 electrons. The C_{60} cages they are regarded as rigid spheres and a bandwidth develop from the weak interactions between the nearest neighbor (n-n) C_{60} cages. In the following, the n-n C_{60} cages interactions are first considered and the force constants along with the phonon frequencies of the fcc lattice are then derived.

2.1. Dispersion Relation in C_{60}

Consider the undoped C_{60} molecule, as a cube with N cages and volume is $Na^3/4$. When the volume is compressed from V to $V + dV$ the work done is:

$$W = (B/2) (\partial V/V) \partial V = B(\partial V)^2 / 2V \quad (1)$$

B being the Bulk modulus and a is the lattice parameter. For a cube $V = a^3$ and $\partial V/V = 3\partial a/a$. Keeping in mind the contribution of 6N bonds between n-n C_{60} cages, W is expressed as

$$W = 3N / k [\partial a / \sqrt{2}]^2 \quad (2)$$

With k is the force constant for n-n cages. A comparison yields, $k = 3Ba / 4$.

A set of C_{60} molecule is treated as a three-dimensional monoatomic lattice with atomic mass and the position of cage as mk and $u \begin{pmatrix} l \\ K \end{pmatrix}$ respectively. The lattice considered S unit cells numbered by an index $l = 1, 2, \dots, S$ and for

masses k ($=1$) [40]. The equations of motion along 110-direction are obtained from force $\partial\Phi / \partial u \begin{pmatrix} l \\ k \end{pmatrix}$ acting on the atom (k) with Φ as the potential energy of the crystal and follows

$$-m_k \ddot{u}_j(k) = K [2u_j(k) - u_{j\pm 1}(k) - u_{j-1}(k)] \quad (3)$$

also

$$-m \ddot{u}_j(l) = K [2u_j(l) - u_{j+1}(l) - u_{j-1}(l)] \quad (4)$$

The equilibrium position of the l^{th} unit cell relative to an origin located at some atom is $r(l) = l_1 a + l_2 b + l_3 c$, where l_1, l_2, l_3 are integers and a, b, c are the primitive translational vectors. Using the plane wave solution as $u_j(l) = A(q) \exp i[q_j r(l) - \omega t]$, with A as the amplitude, q is the wave-vector in 110 direction and $\omega(q)$ is the angular frequency, the dispersion relation reads

$$\omega_L(q) = 2\sqrt{k/m} = \sqrt{3Ba/m} \quad (5)$$

At the zone boundary ($q = \pi/b$). The above is the longitudinal phonon mode, which is due to the rotational motion of the C_{60} molecule.

2.1.1. Dispersion relation in A_3C_{60}

The C_{60} molecule when chemically substituted with alkali metal (K) atoms, the semi conducting C_{60} becomes metallic, at the K_3C_{60} composition and it shows the superconducting nature. With the, doping, K atoms become fully ionized in the C_{60} crystal and give up their electrons to highly polarizable C_{60} molecule. These electrons go to de-localized lowest unoccupied molecular orbital, which can accommodate six electrons. The conduction band is empty for C_{60} crystal and for K_3C_{60} the conduction band is half filled up to the Fermi level. The K atoms were located in two non-equivalents tetrahedral and an octahedral position of the lattice. In doped fullerides, there exists $6N$ C_{60} - C_{60} bonds at a bond distance of $a/\sqrt{2}$, also $8N$ C_{60} - K bonds with bond distance as $a\sqrt{3}/4$ with $a = 14.28 \text{ \AA}$ for K_3C_{60} . In the true sense, a dopant entering in to parent lattice C_{60} tends to expand the lattice for creating a place for itself.

The transfer of charge will certainly result in to some contraction and the final lattice parameter of the doped material will be resultant of these effects. It is noticed that the lattice parameter for K_3C_{60} ($a = 14.28 \text{ \AA}$), Rb_3C_{60} ($a = 14.45 \text{ \AA}$) and Cs_3C_{60} ($a = 14.60 \text{ \AA}$) which are more than the lattice parameter of undoped C_{60} namely, $a = 14.20 \text{ \AA}$ [1] and hence there is a resultant expansion. The total bond energy within the harmonic approximation is expressed as

$$E_B = 6N \frac{\kappa}{2} \left[\frac{a}{\sqrt{2}} - r_{cc} \right]^2 + 8N \frac{\kappa'}{2} \left[\frac{a\sqrt{3}}{4} - r_{mc} \right]^2 \quad (6)$$

with, r_{CC} is the equilibrium C_{60} - C_{60} bond distance (10.04 \AA) and r_{MC} denotes the metal- C_{60} bond distance and is $r_{MC} = (r_{CC}/2) + r_i$, with $r_i = 1.63 \text{ \AA}$ is the ionic radius of K . A relationship in between the force constants K (C_{60} - C_{60}) and K' (M - C_{60}) is established when the total bond energy reach its maximum at the experimental value of lattice parameter a .

Treating K_3C_{60} as a three-dimensional (3D) diatomic lattice with atomic masses as m (M) and positions u (v) for C_{60} (K), the equations of motion follows

$$-m \ddot{u}_j(l) = k [2u_j(l) - u_{j+1}(l) - u_{j-1}(l)] +$$

$$2k_1 [2u_j(l) - v_{j+1/2}(l) - v_{j-1/2}(l)] \quad (7)$$

$$-M \ddot{v}_j(l) = k_1 [2v_j(l) - u_{j+1/2}(l) - u_{j-1/2}(l)] \quad (8)$$

The plane wave solutions are used $u_i(l) = A \exp i[q_j r(l) - \omega t]$ and $v_j(l) = B \exp i [q_j r(l) - \omega t]$ and $k_1 = 0.6 k'$. Following harmonic approximation, all cubic and higher order terms are neglected and also the nearest neighbor interaction naturally demands the force constants and several other parameters in 3D [40]. Confining only for the longitudinal phonon modes of K_3C_{60} along 110-direction, the dispersion relation reads for small q value

$$\omega_+^2 = 4[D_1 + D_2] \cdot D_1 D_2 / [D_1 + D_2] (qb)^2 \quad (9)$$

$$\omega_-^2 = D_1 D_2 / (D_1 + D_2) (qb)^2 \quad (10)$$

Here, $D_1 = [k + (2k'/3)]m^{-1}$ and $D_2 = [k'/3]M^{-1}$. eqn. (9) is an intermolecular optical mode and acoustic characteristics are seen from eqn. (10) in the long-wavelength limit ($q \rightarrow 0$). The developed phonon modes are due to the displacement of C_{60} molecule or K^+ ions in the K_3C_{60} .

2.1.2. Screening Parameter

The phonon mediated interaction is usually treated first and the direct Coulomb interaction is introduced in terms of pseudo potential, μ^* [41,42]. In dealing with a high- T_c superconductor, it is more realistic to first consider the large electron-electron interaction and later the small electron-phonon interaction strength to estimate T_c . The effect of screening of electrons is determined by the renormalized Coulomb repulsive parameter as [41].

$$\mu^* = \mu / [1 + \mu] \ln(\epsilon_F / \omega_{ev}) \quad (11)$$

The cut-off frequency is set equal to the intermolecular optical phonon frequency. Usually, the Coulomb repulsive parameter is obtained

$$\mu = (\Xi/2) \ln [(1 + \Xi/2) / \Xi/2] \quad (12)$$

Here the abbreviation $\Xi^2 = k_s^2 / 4k_F^2$ and $k_s^2 = 6\pi n e^2 / \epsilon_\infty \epsilon_F$.

2.1.3. Electron - Phonon Attractive Parameter

The attractive coupling constant can be calculated from the McMillan formulae [43] which is related through the density of states at fermi level $N(\epsilon_F)$ and the mean square electron-ion matrix and structure calculation of K_3C_{60} using full potential linear muffin-tin orbital [44] method suggest that the superconducting electrons are composed entirely Carbon $2p$, the contribution of $C 2s$ orbital is very small and the largest contributions to $N(\epsilon_F)$ are provided by the $C(3)$ atoms which are the closest to the neighboring C_{60} molecule. The use of McMillan expression is appropriate in K_3C_{60} superconductors for two fold reasons: large density of states as well the more the mass difference of K and C_{60} . The electron-phonon coupling strength λ is

$$\lambda = \frac{N(\epsilon_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (13)$$

$\langle I^2 \rangle$ is a mean square electron-ion matrix element, M the molecular mass and $\langle \omega^2 \rangle$ is an averaged square molecular vibration frequency. The mean square electron-ion matrix element is

$$\langle I^2 \rangle = \left\{ \frac{\Omega}{(2\pi)^3} \int d^3k' [d^3k (k-k')^2 |V(k-k')|^2 \delta(E_k - \varepsilon_F) \delta(E_{k'} - \varepsilon_F)] \right\} \left\{ \frac{\Omega}{(2\pi)^3} \int d^3k \int d^3k' (k-k')^2 \delta(E_k - \varepsilon_F) \delta(E_{k'} - \varepsilon_F) \right\}^{-1} \quad (14)$$

$$\langle I^2 \rangle = \int_0^{2k_F} q^3 dq |V(q)| / \int_0^{2k_F} q dq \quad (15)$$

$V(q)$ being the screened Coulomb potential. In terms of bare Coulomb potential $V_c(q)$ one express, $V(q) = V_c(q)/\varepsilon(q)$. The dielectric function $\varepsilon(q, \omega)$ is

$$\varepsilon(q, \omega) = 1 + \omega_p^2 \left[\frac{q^2 v_F^2}{2} - \omega^2 \right]^{-2} \quad (16)$$

With V_F is the fermi velocity. The static dielectric function $\varepsilon(q)$ in the long-wavelength limit is

$$\varepsilon(q) \approx 4me^2 k_F / \pi \hbar^2 q^2 \quad (17)$$

And the result for screened coulomb potential is

$$V(q) = \frac{4\pi Ze^2 / (q^2 \Omega)}{4me^2 k_F / (\pi \hbar^2 q^2)} \quad (18)$$

$$V(q) = \frac{\hbar^2 \pi^2 Z}{mk_F \Omega} \quad (19)$$

With is Ω is the volume of the cell and Ze denotes effective nuclear charge and is $7e$. Thus, the mean square electron ion matrix element from Eq. (15) follows

$$\langle I^2 \rangle = \left(\frac{\hbar^2 \pi^2 Z}{mk_F \Omega} \right)^2 \int_0^{2k_F} q^3 dq / 2k_F^2 \quad (20)$$

and the electron-phonon coupling strength for the intermolecular vibration frequency $\langle \omega_{er}^2 \rangle$ is

$$\lambda = \frac{2N(\varepsilon_F) [\hbar^2 \pi^2 Z / m\Omega]^2}{M \langle \omega_{er}^2 \rangle} \quad (21)$$

The values of the renormalized Coulomb repulsive parameter and the attractive electron - phonon coupling constant are used while estimating the superconducting and normal state parameters.

3. Discussion and Analysis of Results

The realistic values of some physical parameters are employed following experimental data as follows. The C_{60} molecule is first analyzed using the lattice parameter $a = 14.20 \text{ \AA}$ and $B = 18 \text{ GPa}$ [45]. The effective mass of C_{60} cage is $1.2 \times 10^{-24} \text{ Kg}$ and the force constant κ is obtained as 19.17 N/m . The estimated value of the longitudinal phonon frequency of the C_{60} molecule from eqn. (5) is 42.42 cm^{-1} (5.2 meV). It is worth to mention that this phonon mode comes from $6N$ bonds between n - n cages of C_{60} molecule. Chemical substitution of alkali metal ion in C_{60} molecule introduces extra electrons which are accommodated in the conduction band which is half filled

up to the fermi level and these conduction electrons distort the lattice of K_3C_{60} . The distortion leads to a net expansion as lattice parameter for K doped fullerenes (14.28 \AA) and parent fullerenes is $a = 14.20 \text{ \AA}$. For the evaluation of force constant relationship the total bond energy is then minimized at the experimental value of a ($= 14.28 \text{ \AA}$) for K_3C_{60} to obtain, k' as $0.17k$. It appears that the magnitude of force constant for alkali metal doped fullerenes is larger than the undoped C_{60} . The dispersion relations for the intermolecular phonon modes originate due to the displacement of C_{60} molecule or K^+ ions are then obtained.

The mass of three alkali metals (K) is used as 0.17 amu . The intermolecular alkali C_{60} optic mode (ω_{er}) is obtained as 7.8 meV at $q \rightarrow 0$. The wave vector q ($\approx 2k_F \sin\theta$) can therefore take maximum value up to $2k_F$. For small value of q , the product qb is 10 to deduce the value of acoustic mode as 125.47 meV at $2k_F$. The electron density n ($= 4x3/a^3$) is estimated as $4.12 \times 10^{21} \text{ cm}^{-3}$ from the lattice parameter a of K_3C_{60} and the band structure value of mass as $3.0 m_e$ is used [44]. The fermi energy is obtained as 0.3 eV which is consistent with the earlier data, $\varepsilon_F = 0.2\text{--}0.3 \text{ eV}$ [37]. The other parameters of the electrons are the screening parameter $k_s \cong 0.9 \text{ \AA}^{-1}$ and the fermi wave vector k_F ($\approx 0.5 \text{ \AA}^{-1}$) which are required for the determination of the coulomb repulsive parameter. We have used the value of ε_∞ as 4.4 [46].

The renormalized Coulomb repulsive parameter μ^* is estimated as 0.19 and is attributed to the fact that ε_F is higher at least an order of magnitude with the intermolecular alkali C_{60} optic phonon frequency. The electron-phonon coupling strength (λ) using eq. (21) is obtained as 1.2 . We note that the dimensionless electron-phonon coupling strength as estimated by Gunnarson is about $0.5\text{--}1$ [8]. Quite generally, the moderately large value of Coulomb repulsive parameter is appropriate for a narrow band width material on the metallic side of a metal-insulator transition. one can see that in dealing with K_3C_{60} fullerenes the coupling strength ($\lambda > 1$) and the renormalized coulomb repulsive parameter $\mu^* = 0.19$ for the characteristic phonon frequency ($\omega_{er} = 7.84 \text{ meV}$) is believed to distort the lattice leading to a superconducting state.

3.1. Transition Temperature

In the regime $\lambda > 1$ the strong coupling theory [47] applies and the transition temperature T_c , for K_3C_{60} is estimated following

$$T_c^{er} = 0.25 \omega_{er} [\exp(2/\lambda_{eff}) - 1]^{-1/2} \quad (22)$$

Where

$$\lambda_{eff} = (\lambda - \mu^*) [1 + 2\mu^* + \lambda\mu^* t(\lambda)]^{-1} \quad (23)$$

$$t(\lambda) = 1.5 \exp(-0.28 \lambda) \quad (24)$$

The effective coupling constant λ_{eff} is deduced as 0.62 for the numerical function $t(\lambda)$ value 1.07 with $\lambda, = 1.2$ and T_c^{er} is estimated as $\cong 5K$ which is much lower than the reported experimental data [1] of about $18K$. The above approach with intermolecular phonons does not explain a medium T_c , in K_3C_{60} and hence it is important to look for the role of intramolecular phonons to assess the reported value. The role of collective excitation mechanism over

conventional phonon mechanism in cuprates was earlier successfully explained with a generalized expression for T_c in a strong coupling theory [47]. The critical temperature T_c is obtained by both intermolecular and intramolecular phonons in fullerides as

$$T_c = T_c^{er} [\omega_{ra} / T_c^{er}]^\eta \quad (25)$$

with

$$\eta = \lambda_{ra} / (\lambda_{ra} + \lambda_{er}) \quad (26)$$

λ_{ra} being the intramolecular coupling constant and is obtained as 0.4 from the scattering time ($\tau = 1.2 \times 10^{-14}$ sec) as

$$\lambda_{ra} = \hbar / (2\pi k_B T \tau) \quad (27)$$

We use the reported value of $\omega_{ra} = 1012 \text{ cm}^{-1}$ from the earlier data [1], T_c is obtained as 22 K. The strength of coupling $\sigma = \lambda_{er} / \lambda_{ra}$ is 3.0. From the analysis of superconducting T_c , it is natural to make two comments the high-energy intramolecular phonons are moderately coupled while to that to the low energy intermolecular phonons are strongly coupled to neighboring electrons and T_c , mainly arises from the significant contribution of intramolecular phonons. The dimensionless Coulomb repulsive parameter μ^* is therefore believed to severely reduced and attributed to the scaling factor $\ln[\varepsilon_F/\omega_b]$ appeared in denominator of the expression of μ^* . As the fermi energy is larger at least an order of magnitude by intermolecular phonons, the retardation effects are expected to be very small. Generally, energy ω_b is presented as characterizing bosons (ω_{er} , or ω_{ra}), but opinion about its choice in screening is far from being unanimous. The only thing one must be sure of is that, if a boson is a candidate for superconductivity, one must expect $\mu^* < \mu \sim 0.5$ and of course $\lambda - \mu^* > 0$. To obtain some specific results, we obtain numerical results for the transition temperature with coupling parameters and are presented in the following plots for various conditions. In Figure 1, we show the result for T_c as a function of μ up to 0.3 for a set of parameters $\lambda_{er} = 1.2$ and $\lambda_{ra} = 0.4$. The analytic expression for T_c from eq. (22) clearly demonstrates that T_c , is strongly influenced by the Coulomb repulsive parameter and is higher for small values of μ . For a set of coupling parameters $\mu^* = 0.19$, $\lambda_{er} = 1.2$ and $\lambda_{ra} = 0.4$ and T_c , of 22 K is calculated.

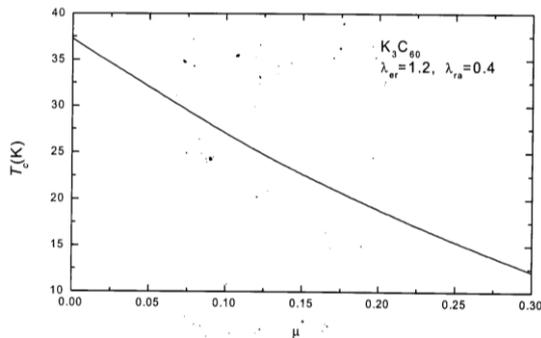


Figure 1. Variation of T_c with μ^*

The present study is essentially based on the application of strong coupling theory with an additional pairing force, we have feeling that such studies describe the dependence of T_c , on different coupling strengths, which has not been

tested carefully and is definitive to impose any constraints on theoretical approaches. An important feature of eq. (22) is displayed in Figure 2. We plot T_c , as a function of λ_{er} up to 2.0 for a set of parameters $\mu^* = 0.19$ and $\lambda_{ra} = 0.4$. It is noticed from the curve that T_c , increases initially with the enhanced value T_c . For the above set of parameters, if the present system is strongly coupled then one can achieve the higher values of T_c . The values of coupling parameters as $\lambda_{er} (= 1.2)$, $\lambda_{ra} (= 0.4)$ and $\mu^* = 0.19$ are quite reasonable in view of fullerides superconductors. We also investigate the effect of the intramolecular phonon coupling strength on T_c . In Figure 3 the variation of T_c for different values of λ_{ra} , varying from 0.0 to 0.7 is presented. In plotting this curve we take $\lambda_{er} = 1.2$ and $\mu^* = 0.19$.

We see from this graph that T_c , is highly sensitive to λ_{ra} even for moderate coupling. We now focus on the relationship in between λ_{er} and μ^* within the present formalism for K_3C_{60} superconductors. We plot the variation of λ_{er} with μ^* in Figure 4. For lower values of λ_{er} , yields unphysical values for a set of parameters ($T_c = 22 \text{ K}$ and $\lambda_{ra} = 0.4$).

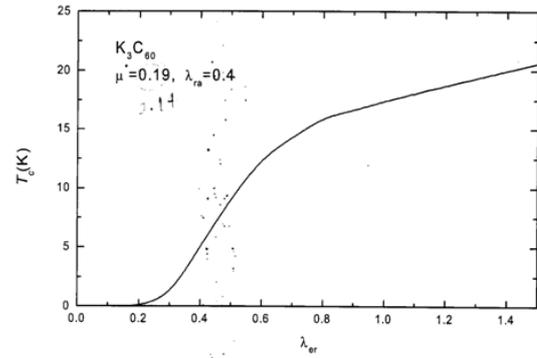


Figure 2. Variation of T_c with λ_{er}

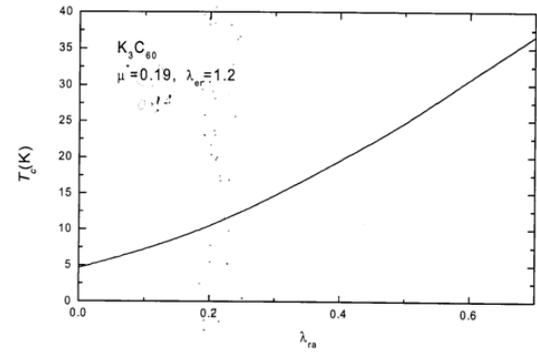


Figure 3. Variation of T_c with λ_{ra}

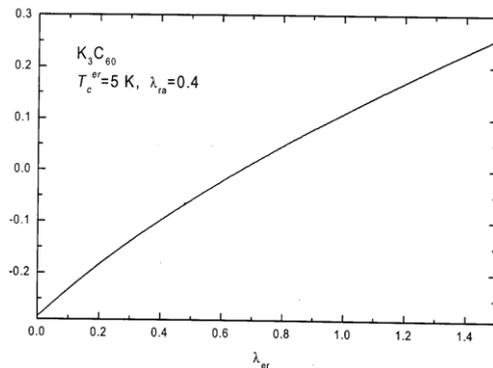


Figure 4. Variation of λ_{er} with μ^*

Within the present approach the intermolecular phonons must be strongly coupled. Higher and positive μ^* implies a constant repulsive interaction that is insufficient to create a superconducting state despite of the additional coupling of intramolecular phonons apart from electron-intermolecular phonon interactions.

3.1.1. Isotope Effect Coefficient

The isotope effect coefficient is

$$\alpha = (0.5)(d \ln T_c / d \ln \omega) \quad (28)$$

From eq. (22) and (28) and the ω dependence of T_c is introduced in terms of μ^* following the relation $\mu^* d \ln \omega = d \ln \mu$, leads to the following result of isotope effect coefficient as

$$\alpha = \{1 - \mu^{*2}[1 + 2\lambda + \lambda^2 t(\lambda)] / \lambda_{eff}(\lambda - \mu^*) [1 + (4T_c/\omega)^2]\} / 2 \quad (29)$$

Here ω is the average phonon frequency. The mass of carbon directly influences the intermolecular phonon frequency, as $\omega_{er} \sim [mM / (m + M)]^{1/2}$ with m (M) mass of C_{60} (K) and a finite value of carbon isotope effect is expected. Equation (29) yields $\alpha \cong 0.24$ which is slightly lower than the reported value of $\alpha = 0.30 \pm 0.06$ with 100% substitution of ^{13}C for ^{12}C [15] and consistent with results of Fuhrer et al. [16]. The reduced inter fullerene mass $[mM/(m + M)]^{1/2}$ is definitely small in comparison with the intra fullerene mass $[(m + M)/2]$, the carbon isotope exponent essentially causes the change in intermolecular phonon frequency and thus it is argued that although intramolecular phonons do play a significant role, however the participation of intermolecular phonons can not be ignored. Figure 5 shows the variation of estimated isotope effect from Eq. (29) with screening parameter. It is noticed that the BCS one half value is recovered for it $\mu^* = 0.0$. With the increase in μ^* values the isotope effect exponent decreases for $\lambda_{er} = 1.2$ and $\lambda_{ra} = 0.4$. However, a reliable alkali metal isotope effect is not reported for K_3C_{60} system, but a negative α_{Rb} is documented [18] that necessarily ruled out the possibility of participation of intermolecular phonons. The justification lies in a fact that the ratio α_c/α_k depends on the weights of on ball carbon and carbon alkali metal dominated phonon modes that are sensitive to λ and μ^* .

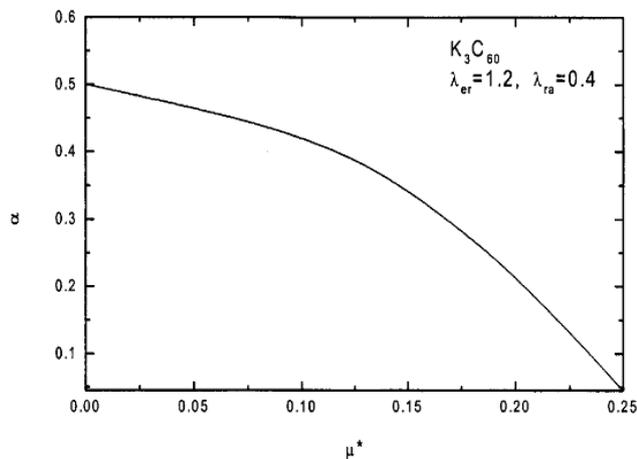


Figure 5. Variation of α with μ^*

3.1.2. Energy Gap Parameter

The energy gap parameter β [30] is

$$\beta \cong 2 \Delta(0) / k_B T_c = 3.25 [1 + 5 (T_c/\omega)^2 \ln(\omega/T_c)] \quad (30)$$

Where $\Delta(0)$ is the energy gap at zero temperature. The energy gap parameter provides a measurement of coupling strength for phonon mediated electron-electron interaction. Substantial doubts arise on tunneling measurement data [21], which predicts significantly higher values of β in K_3C_{60} fullerides. The energy gap parameter ($\beta \cong 3.68$) is estimated using ω_{er} as 63.25 cm^{-1} and T_c of about $5K$ from eq. (30). The magnitude of energy gap is larger than the BCS limit of 3.53 and thus indicates the strong coupling regime. On the other hand, the gap parameter when intramolecular phonons are considered in the pairing mechanism is estimated as 3.54 which is close to the BCS limit where the values $\omega_{ra} = 1012 \text{ cm}^{-1}$ and $T_c = 22K$ are used. This implies that, the intramolecular phonons requires weak interactions with the conduction electrons and is consistent with the infrared spectroscopy [22], muon spin relaxation rate measurements [23], nuclear spin relaxation measurements [25] which strongly favors the participation of intramolecular phonons in the pairing mechanism. Furthermore, the absolute reflectivity measurements [24] on K_3C_{60} reports $\beta = 3.6 \sim 4.0$, which is similar to BCS weak coupling limit and the electron-phonon coupling strength cannot be as large as 2.

3.1.3. Pressure Effect on Transition Temperature

In order to analyze the pressure dependence of T_c , for K_3C_{60} system, we begin with the earlier developed Eqn. (25) according to which,

$$\frac{d \ln T_c}{dP} = \left[1 - \frac{\lambda_{ra}}{\lambda_{er} + \lambda_{ra}} \right] \frac{d \ln T_c^{er}}{dP} + \left[\ln \omega_{ra} - \ln T_c^{er} \right] \frac{d}{dP} \left[\frac{\lambda_{ra}}{\lambda_{er} + \lambda_{ra}} \right] + \left[\frac{\lambda_{ra}}{\lambda_{er} + \lambda_{ra}} \right] \frac{d \ln \omega_{ra}}{dP} \quad (31)$$

Keeping in mind that C_{60} molecules are extremely rigid and hence pressure neglecting the pressure induced effects of intramolecular phonons,

$$\frac{d \ln \omega_{ra}}{dP} = \frac{d \omega_{ra}}{dP} = 0 \quad (32)$$

Henceforth, we rewrite eq. (31) as:

$$\frac{d \ln T_c}{dP} = \left[1 - \frac{\lambda_{ra}}{\lambda_{er} + \lambda_{ra}} \right] \frac{d \ln T_c^{er}}{dP} + \frac{1}{(\lambda_{er} + \lambda_{ra})^2} \left[\ln \left(\frac{\omega_{ra}}{T_c^{er}} \right) \right] \left[\lambda_{er} \frac{d \lambda_{ra}}{dP} - \lambda_{ra} \frac{d \lambda_{er}}{dP} \right] \quad (33)$$

Furthermore,

$$\frac{d \ln T_c^{er}}{dP} = \frac{\partial \ln T_c^{er}}{\partial \lambda} \frac{d \lambda_{er}}{dP} + \frac{\partial \ln T_c^{er}}{\partial \omega_{er}} \frac{d \omega_{er}}{dP} + \frac{\partial \ln T_c^{er}}{\partial \mu^*} \frac{d \mu^*}{dP} \quad (34)$$

Using eq. (22), we get the following results:

$$\frac{\partial \ln T_c^{er}}{\partial \lambda} \frac{d\lambda_{er}}{dP} = D_{11} \frac{d \ln \lambda_{er}}{dP} \quad (35)$$

Where

$$D_{11} = \frac{\lambda(1+2\mu^*+1.07\mu^{*2})}{(\lambda-\mu^*)^2} \left[1 + \left\{ \exp\left(\frac{2+4\mu^*+2.14\lambda\mu^*}{\lambda-\mu^*}\right) \right\}^{-1} + \left\{ \exp\left(\frac{2+4\mu^*+2.14\lambda\mu^*}{\lambda-\mu^*}\right) \right\}^{-2} \right] \quad (36)$$

We use the following

$$\frac{\partial \ln T_c^{er}}{\partial \omega_{er}} \frac{d\omega_{er}}{dP} = \frac{d \ln \omega_{er}}{dP} \quad (37)$$

And

$$\frac{\partial \ln T_c^{er}}{\partial \mu^*} \frac{d\mu^*}{dP} = D_{12} \frac{d \ln \mu^*}{dP} \quad (38)$$

$$D_{12} = \frac{-\mu^*(1+2\lambda+1.07\lambda^2)}{(\lambda-\mu^*)^2} \left[1 + \left\{ \exp\left(\frac{2+4\mu^*+2.14\lambda\mu^*}{\lambda-\mu^*}\right) \right\}^{-1} + \left\{ \exp\left(\frac{2+4\mu^*+2.14\lambda\mu^*}{\lambda-\mu^*}\right) \right\}^{-2} \right] \quad (39)$$

Combining these, we write

$$\frac{d \ln T_c^{er}}{dP} = D_{11} \frac{d \ln \lambda_{er}}{dP} + \frac{d \ln \omega_{er}}{dP} + D_{12} \frac{d \ln \mu^*}{dP} \quad (40)$$

Here, in first and the third term are dependent on the variation of the $N(\epsilon_F)$ with pressure. In order to make progress, we have used the value $B = 13.18 \text{ GPa}$ and $\epsilon_F = 0.31 \text{ eV}$ as documented in the previous section. The free electron gas result $d \ln N(\epsilon_F)/dP = (-2/3) \kappa_T$, where κ_T ($\sim B^{-1}$) is thermal compressibility. The calculated value of $d \ln N(\epsilon_F)/dP$ is about $-5.058 \text{ } (\text{GPa})^{-1}$. However, Kerkoud and coworkers reported a rate of about $\sim -10 \text{ } (\text{GPa})^{-1}$ from NMR technique [48] although of limited accuracy. From eq. (11) and (13), we write

$$\frac{d \ln \mu^*}{dP} = \frac{d \ln N(\epsilon_F)}{dP} \left(\frac{\mu^*}{\mu} \right) - \mu^* \left[\frac{2d \ln \omega_p}{dP} - \frac{d \ln N(\epsilon_F)}{dP} - \frac{d \ln \omega_{er}}{dP} \right] \quad (41)$$

$$\frac{d \ln \lambda_{er}}{dP} = \frac{d \ln N(\epsilon_F)}{dP} - \frac{d \ln \langle \omega_{er}^2 \rangle}{dP} \quad (42)$$

Here the pressure dependence of the quantity $\langle I^2 \rangle$ has been neglected. Using eq. (41) and (42) into eq. (40), we obtain:

$$\frac{d \ln T_c^{er}}{dP} = \left[D_{11} + D_{12} \left(\frac{\mu^*}{\mu} \right) + D_{12\mu^*} \right] \frac{d \ln N(\epsilon_F)}{dP} + [1 + D_{12\mu^*} - 2D_{11}] \frac{d \ln \langle \omega_{er}^2 \rangle}{dP} - 2D_{12\mu^*} \frac{d \ln \omega_p}{dP} \quad (43)$$

Here, we assume: $d \ln \lambda_{rd}/dP \approx d \ln N(\epsilon_F)/dP$, $d \ln \langle \omega_{er}^2 \rangle /dP \approx 2d \ln \langle \omega_{er} \rangle /dP$ and $d \ln \langle \omega_{er} \rangle /dP \approx d \ln \langle \omega_{er} \rangle /dP$. The free electron estimate for $d \ln \omega_p/dP = 1/2B$ yields a value of about $3.79 \text{ } (\text{GPa})^{-1}$. We follow $\gamma_G = B d \ln \langle \omega \rangle /dP$ to obtain $d \ln \omega_{er}/dP = 15.17 \text{ } (\text{GPa})^{-1}$, using $\gamma_G = +2$ as earlier reported [35]. The parameters needed for further calculations are obtained as $D_{11} = 1.7$ and $D_{12} = -0.96$ from the value of $\lambda = 1.2$, $\mu = 0.75$ and $\mu^* = 0.19$. Using Eqn's (33-43) we find the value of $d \ln \mu^*/dP$

$= -0.78 \text{ } (\text{GPa})^{-1}$, $d \ln \lambda_{er}/dP = -35.39 \text{ } (\text{GPa})^{-1}$, $d \ln \lambda_{rd}/dP = -5.05 \text{ } (\text{GPa})^{-1}$, $d \ln T_c^{er}/dP$ is $-45.64 \text{ } (\text{GPa})^{-1}$, $d \ln T_c/dP = -39.60 \text{ } (\text{GPa})^{-1}$ and slope $dT_c/dP = -8.7 \text{ K/GPa}$ which is consistent with the earlier reported value [34] of -7.8 K/GPa . Figure 6 shows the variation of T_c with pressure along with the experimental data.

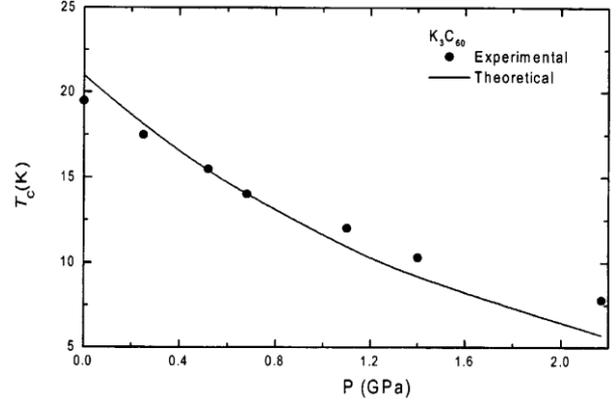


Figure 6. Variation of T_c with Pressure. Closed circles represents the experimental data taken from Spam et al. (1992)

For fitting of the data we have employed the relation $T_c(P) = T_c(0) \exp[-0.3\gamma p]$ using $\gamma_G = +2$ [35]. We follow the discussion and results of Spam et al. [34], who fit the data by using $T_c(P) = T_c(0) \exp[-\gamma p]$ with $\gamma = 0.44 \pm 0.03 \text{ GPa}^{-1}$. We therefore reach the conclusion that the logarithmic derivative of the Coulomb pseudo potential with pressure, $d \ln \mu^*/dP$, is smaller as compared to the other logarithmic derivatives involved in the expression of superconducting transition temperature as we dealt with. The variation of T_c with pressure is thus dependent on the variation of the density of states at fermi level, the coulomb pseudo potential and the variation of the characteristic phonon frequency with pressure.

3.1.4. Volume Dependent Transition Temperature

We now explore our efforts in studying the volume derivative of T_c , or dT_c/dV . Such studies point to either weak or strong coupling of mediating bosons. We note that due to extremely rigidity of C_{60} the compression contracts the weak intermolecular bonds and high-energy intramolecular bonds are unaffected. With these considerations, the eq. (25) simplifies to the following relation,

$$\frac{dT_c}{dV} = T_c^{er} \frac{d}{dV} \left[\frac{\omega_{ra}}{T_c^{er}} \right]^\eta + \left[\frac{\omega_{ra}}{T_c^{er}} \right]^\eta \frac{dT_c^{er}}{dV} \quad (44)$$

Leads to the following result

$$\frac{dT_c}{dV} = (1-\eta) \left[\frac{\omega_{ra}}{T_c^{er}} \right]^\eta \frac{dT_c^{er}}{dV} \quad (45)$$

With an assumption that intramolecular phonons are independent in any change of the volume [49],

$$\frac{d \ln \omega_{ra}}{dV} = \frac{d \omega_{ra}}{dV} = 0 \quad (46)$$

Following eq. (22), we write

$$\frac{dT_c^{er}}{dV} = \frac{0.25}{[\exp(2/\lambda_{eff}) - 1]^{1/2}} \times \frac{d\omega_{er}}{dV} + \frac{\exp(2/\lambda_{eff})}{[\exp(2/\lambda_{eff}) - 1]^{3/2}} \times \left(\frac{0.25\omega_{er}}{\lambda_{eff}^2} \right) \frac{d\lambda_{eff}}{dV} \quad (47)$$

Where,

$$\frac{d\lambda_{eff}}{dV} = \frac{(1+3\mu^{*2} + \lambda\mu^*t(\lambda)^2) d\lambda_{eff}}{[1+2\mu^* + \lambda\mu^*t(\lambda)]^2} + \frac{(\lambda\mu^* - \mu^*\lambda^2)}{[1+2\mu^* + \lambda\mu^*t(\lambda)]^2} \frac{dt(\lambda)}{dV} \quad (48)$$

Now, we obtain,

$$\frac{dT_c}{dV} = D_{21} \frac{d\omega_{er}}{dV} + D_{22} \frac{d\lambda_{er}}{dV} + D_{23} \frac{dt(\lambda)}{dV} - D_{24} \frac{d\mu^*}{dV} \quad (49)$$

Here, we define

$$D_{21} = V_{00} \left\{ \frac{0.25}{(\exp(2/\lambda_{eff}) - 1)^{1/2}} \right\} \quad (50)$$

$$D_{22} = V_{00} \left\{ \frac{(\exp(2/\lambda_{eff}))}{(\exp(2/\lambda_{eff}) - 1)^{3/2}} \times \frac{0.25\omega_{er}}{\lambda_{eff}^2} \right\} \frac{(1+2\mu^* + \mu^{*2}t(\lambda))}{(1+2\mu^* + \lambda\mu^*t(\lambda))^2} \quad (51)$$

$$D_{23} = V_{00} \left\{ \frac{(\exp(2/\lambda_{eff}))}{(\exp(2/\lambda_{eff}) - 1)^{3/2}} \times \frac{0.25\omega_{er}}{\lambda_{eff}^2} \right\} \frac{(\mu^*\lambda - \mu^*\lambda^2)}{(1+2\mu^* + \lambda\mu^*t(\lambda))^2} \quad (52)$$

and

$$D_{24} = -V_{00} \left\{ \frac{(\exp(2/\lambda_{eff}))}{(\exp(2/\lambda_{eff}) - 1)^{3/2}} \times \frac{0.25\omega_{er}}{\lambda_{eff}^2} \right\} \frac{(1+2\lambda + \lambda^2t(\lambda))}{(1+2\mu^* + \lambda\mu^*t(\lambda))^2} \quad (53)$$

Where

$$V_{00} = (\omega_{ra}/T_c^{er}) \frac{\lambda_{ra}}{\lambda_{er} + \lambda_{ra}} \left(1 - \frac{\lambda_{ra}}{\lambda_{er} + \lambda_{ra}} \right) \quad (54)$$

Furthermore, the logarithmic volume derivative of the coupling parameter λ follows:

$$\frac{d \ln \lambda}{d \ln V} = B \frac{d \ln N(\varepsilon_F)}{dP} + 2\gamma_G \quad (55)$$

Leads to the ratio

$$\Phi = \frac{d \ln \lambda}{d \ln V} \quad (56)$$

With the values of B , $d \ln N(\varepsilon_F)/dP$ and $d \ln \langle \omega \rangle / dP$ discussed earlier, we find $\Phi = 3.3$ for K_3C_{60} . In passing we note that the value of Φ for AMIF is comparable to the value of $\Phi = 3.7$ for usual metals as Al [49].

The physical significance of the volume derivative of T_c we estimate the parameters as $D_{21} = 0.16$, $D_{22} = 70.6$, $D_{23} = -2.7$ and $D_{24} = -323$ from the earlier mentioned values of various coupling strengths. Looking to eq. (49), dT_c/dV is being influenced by volume dependence of screening parameter, volume dependence of intermolecular vibration mode, volume dependence of intermolecular phonon coupling strength and the intramolecular phonon frequency as well various coupling parameters are independent of volume. We note that the Coulomb repulsion suppresses T_c as is being noticed from Figure 1.

Henceforth, the contribution to dT_c/dV proportional to $d\mu^*/dV$ is negative. We follow Crespi and Cohen [49] who argues that the logarithmic dependence of μ^* on ε_F points to the fact that volume derivative of μ^* is small in magnitude. A natural argument follows that the volume derivative of $t(\lambda)$ and of μ^* is small in comparison to $d\lambda/dV$, henceforth we neglect these two terms in eq. (49).

4. Conclusion

In this paper, we have devoted our efforts in revealing the attractive pairing mechanism and various physical parameters of alkali metal intercalated fullerenes superconductor within the framework of strong coupling theory. The particular system chosen for the study, because huge experimental data is available and consistent explanation is timely needed. Considering the three dimensional K_3C_{60} as a diatomic lattice of K and C_{60} , we derive expression for intermolecular (acoustic and optical) phonon modes. We have properly used the Bulk modulus as well as other structural parameters. The intermolecular optical phonon frequency obtained and used frequency of intramolecular phonons is consistent with the recent theoretical and experimental findings. We exercised the superconducting state parameters i.e. the transition temperature (T_c), the carbon isotope effect (α), the energy gap parameter (β) and the pressure as well volume effect on T_c describing the superconducting state in alkali metal intercalated fullerenes superconductors.

The calculated value of T_c , α , β and dT_c/dP are consistent with the reported data. The deduced value of coupling strength for the intermolecular phonons (optical) favours the strong coupling mechanism. By understanding that intramolecular phonons indeed do play a significant role, we have obtained a steep increase in T_c . Unlikely the coupling strength for intramolecular phonons is an indicative of weak coupling theory. Various reports strongly favours the intramolecular vibrations as a key source of superconductivity and claim that intermolecular phonons will not induce the state, still we believe and argue that both the inter and intramolecular phonons participate in the superconducting state as well is essential for superconducting fullerenes superconductors.

We argue that the reduced value of α essentially points to the large Coulomb repulsion apart from large electron-phonon coupling strength. Deduced results on α and β are consistent with the earlier reported data's. It is inferred that electron pairing with intermolecular phonons would lead to a strong coupling while to that the intramolecular phonons require weak coupling mechanism. Although several reports strongly favours the intramolecular vibrations as a key source of superconductivity and claim that intermolecular phonons will not induce the state, the present analysis reveals that both the inter- and intramolecular phonons participate in the superconducting state.

We also discuss the pressure dependence of dT_c/dP . We appeal from the model calculations that the pressure dependence of T_c demonstrates the metallic behaviour. The appreciation reveals that the developed expression yields a value of dT_c/dP close to the reported data. The variation of T_c with pressure is thus dependent on the variation of the fermi level density of states, the Coulomb

pseudo potential and the variation of the phonon frequency with volume. The pressure effect in AMIF is huge and pressure derivative of T_c is negative, while to that volume derivative of T_c is positive.

Finally, the electron pairing in fullerides superconductors and a consistent interpretation of the properties describing superconducting state as transition temperature, carbon isotope effect, energy gap parameter, pressure and volume effect on T_c , describing the superconducting state reveals the fact that both, the Coulomb and electron-phonon (inter- and intramolecular) are important in examining the unusual physical properties in alkali metal intercalated fullerides superconductors.

Acknowledgement

The author (Daluram Yadav) is gratefully acknowledge to Dr. N. Kaurav for valuable discussion.

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