

Isotope Effect Exponent in Rb_3C_{60} Fullerides

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Abstract- The studies of the superconducting properties of fullerenes are briefly reviewed. The calculations are compared with coupling constants deduced from a number of different experimental techniques. Estimates of the Coulomb pseudo potential μ^* and isotope exponent α describing the effect of the Coulomb repulsion on the superconductivity, as well as possible electronic mechanisms for the superconductivity, are reviewed. The influence of inter and intramolecular phonons on the nature of pairing mechanism and the superconducting state parameters of alkali metal intercalated fullerenes is investigated using the strong coupling theory. It is shown that the electrons in the unfilled band of C_{60} develops due to intercalation of alkali metal distort the Rb_3C_{60} lattice and yield low energy intermolecular vibrations. The incorporation of the intramolecular phonons in the transition temperature enhances to about 33 K.

Keywords: Inter and Intramolecular Phonons, Fullerenes, Coulomb Pseudo potential, Transition temperature.

I. INTRODUCTION

A new family of huge molecular structure high temperature superconductors does not come along every day. The high transition temperature of superconductors continues to resist explanation. Theories about, but decisive experimental tests do not. Significant clues would be available from measurements of the dependence of T_c on the isotope exponent of materials. Remarkable discovery in alkali metal intercalated fullerenes, A_3C_{60} ($A = K, Rb, Cs$) $T_c \approx 18$ to 45 K [1] have initiated research to elucidate origin of high - T_c in non metal oxides. The large transition temperature T_c and enhances density of states of fullerenes [2] in comparison to conventional superconductors have posed a serious query of electron pairing, whether it can be solely obtained within BCS framework or some other mechanism is required.

The phonon spectrum in fullerenes have a wide frequency range and is broadly classified in two regions, one belongs to rotation of C_{60} molecule and intermolecular vibrations in range of 50 to 150 cm^{-1} while other are intramolecular mode with frequency 400 to 1400 cm^{-1} the nature of electron pairing mechanism in alkali metal intercalated fullerenes requires an understanding of detailed phonon spectrum as well as electron - phonon coupling strength to decide whether or not electron pairing is a consequence of virtual phonons. The characteristic parameters of superconducting state as isotope exponent impose constraints on any mechanism. In particular, carbon isotope effect [3] depicts $\alpha = 0.3 \pm 0.06$ (0.37 ± 0.05) with 100 (75 ± 5) % substitution of ^{13}C for ^{12}C in $K(Rb)_3C_{60}$, which indicate participation of optical phonons in pairing. Subsequent measurement of

T_c in Rb_3C_{60} yield $\alpha = -0.028 + 0.03$, a result which implies that intermolecular optical phonon plays at most a minor role [4].

The reduced carbon isotope effect places constraints on weak coupling theory of phonons, as in BCS theory α is 0.5. Several other reports such as magnetic susceptibility data [3], nuclear relaxation measurements [5] and carbon isotope effect studies [6] emphasis the participation of intramolecular vibrational modes. Although these studies point towards phonon mechanism but a departure from weak coupling BCS theory is clearly depicted. While exploring the nature of superconducting state the knowledge of characteristic energy of the intermediately boson in the phonon mediated pairing interaction is an important factor in determining whether weak or strong coupling is appropriate. It is widely believed that the high frequency ($\sim 400 - 1400$ cm^{-1}) intramolecular modes or electronic excitation would tend to favours the weak coupling theory while intermolecular modes (~ 150 cm^{-1}) would require normally strong coupling theory.

This motivates us to address ourselves to the question of understanding the transition temperature of fullerenes taking into account of both intermolecular and intramolecular phonons. In the alkali metal intercalated fullerenes, the intermolecular vibrations possess the energy in the range 2.5 to 25 meV and the Fermi energy (ϵ_F) is about 0.2 ~ 0.3 eV. Thus in fullerenes $\omega_{er} < \epsilon_F$, so the consideration of intermolecular vibrations, i.e., the coupling of the conduction electrons with the intermolecular phonons will be reasonable as a good starting point. In the problem of

fullerenes, we do believe that the coupling of conduction electrons with the displacements of C_{60} molecule or the alkali ions will induce the superconductivity.

Indeed the phonon interaction, as the carbon isotope effect is present in the superconducting phase of Rb_3C_{60} . however, the coupling parameters are small for the intramolecular vibrations to produce high T_c , we have introduced the coupling of conduction electrons with the intramolecular phonons and believe that our results are of considerable interest in yielding a superconducting state as well as explain the attractive pairing mechanism. 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} [7] and the birth of a new family of organic superconductors based on aromatic molecules, as doped picene [8], phenanthrene [9], coronene [10] and dibenzopentacene.

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 [1]. Nonetheless, the anomalous properties of “expanded” fullerides with large intermolecular distance, like ammoniated compounds [11] 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 *A-15* structure, with a bipartite lattice [7, 12]. *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 [13], as opposed to K_3C_{60} and Rb_3C_{60} , which are superconductors in the same conditions.

II. METHODOLOGY

When C_{60} molecule chemically substituted with alkali metal atoms, the semiconducting C_{60} becomes metallic, at A_3C_{60} composition and it shows superconducting nature. With doping *A* atoms become fully ionized C_{60} crystal and give up their electrons to highly polarizable C_{60} molecule. These electrons go to delocalized lowest unoccupied orbitals, which can accommodate six electrons. *A* atoms were located in two non - equivalents tetrahedral and an octahedral position of the lattice. In doped fullerenes, there exists $6N$ $C_{60} - C_{60}$ bonds at a bond distance of $a/\sqrt{2}$, also $8N$ $C_{60} - A$ bonds with bond distance as $a/\sqrt{3}/4$ with $a = 14.45$ Å for Rb_3C_{60} .

The total bond energy within the harmonic approximation is expressed as

$$E_B = 6N \frac{\kappa}{2} \left[\frac{a}{\sqrt{2}} - r_{cc} \right]^2 + 8N \frac{\kappa'}{2} \left[\frac{a\sqrt{3}}{4} - r_{mc} \right]^2 \quad (1)$$

r_{cc} is being the equilibrium $C_{60} - C_{60}$ bond distance (10.04 Å) and r_{mc} denotes the metal - C_{60} bond distance. Treating Rb_3C_{60} as a 3D diatomic lattice with atomic masses as m (M) and positions u (v) for C_{60} (A), the equations of motion follows

$$-m\ddot{u}_j(lk) = \kappa [2u_j(lk) - u_{j+1}(lk) - u_{j-1}(lk)] + \frac{4\kappa'}{3} [2u_j(lk) - v_{j+1/2}(lk) - v_{j-1/2}(lk)] \quad (2)$$

and

$$-M\ddot{v}_j(lk) = \frac{2\kappa'}{3} [2v_j(lk) - u_{j+1/2}(lk) - u_{j-1/2}(lk)] \quad (3)$$

For various symmetries in Rb_3C_{60} , several rotational and vibrational transverse and longitudinal frequencies will be then obtained from the 3D dynamical matrix and are rigorous which indeed not the scope of the present analysis is confining only for the longitudinal phonon modes along 110-direction, the dispersion relation

$$\omega_+^2 = 4[D_1 + D_2] - D_1 D_2 [D_1 + D_2]^{-1} (qb)^2, \quad (4)$$

$$\omega_-^2 = D_1 D_2 [D_1 + D_2]^{-1} (qb)^2. \quad (5)$$

Here, $D_1 = [\square + (2\square\square/3)] m^{\square 1}$ and $D_2 = [\square\square/3] M^{\square 1}$. Eqn. (4) is an intermolecular optical vibrational mode and vibrational acoustic characteristics are seen from Eqn. (5) in the long-wavelength limit.

III. SUPERCONDUCTING STATE PROPERTIES

Electron - Phonon interaction parameter

Evaluation of transition temperature T_c requires attractive electron - phonon coupling constant and coulomb repulsive parameter. Effect of screening of electrons is determined by renormalized coulomb repulsive parameter [14] is

$$\mu^* = \mu / [1 + \mu \ln (\epsilon_f / \omega_e)] \quad (6)$$

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

$$\mu = \xi^2 \ln [(1 + \xi^2) / \xi^2] \quad (7)$$

Here the abbreviation $\xi^2 = k_s^2 / 4k_F^2$ and $k_s^2 = 6\pi n e^2 / \epsilon_f$.

The electron-phonon coupling strength λ [15] is

$$\lambda = \frac{N(\epsilon_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (8)$$

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

Thus, the mean square electron ion matrix element reads

$$\langle I^2 \rangle = \left(\frac{\hbar^2 \pi^2 Z}{m k_F \Omega} \right)^{2k_F} \int_0^{2k_F} q^3 dq / 2k_F^2 \quad (9)$$

And the electron-phonon coupling strength [16] for the vibrational phonons as

$$\lambda = \frac{2N(\epsilon_F)[\hbar^2 \pi^2 Z / m \Omega]^2}{M \langle \omega_{er}^2 \rangle} \quad (10)$$

With Ω is the volume of the cell and Ze denotes effective nuclear charge and is $7e$. 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.

Transition temperature T_c

It was pointed out that the estimated values of the electron-phonon coupling λ to the intramolecular modes are of the right order of magnitude to explain the transition temperature T_c . Since the calculated values of λ are only intermediate, the quite high intramolecular phonon frequencies are important for the explanation of the rather high values of T_c . For values of λ in the upper range of the estimates, the rather large values of T_c can be understood even if it is assumed that the inefficient renormalization of μ^* by retardation effects in the fullerenes.

The total bond energy is minimized at the experimental value of a for Rb_3C_{60} superconductor to obtain, κ' as 1.1κ . The intermolecular alkali C_{60} optic mode is 21.35 meV. For small value of q , the product qb is 10 to deduce acoustic mode as 13.55 meV. The Fermi energy is obtained as 0.46 (0.25) eV. The other parameters of electrons are k_s ($\approx 2.1 \times 10^8$ cm⁻¹) and k_F ($\approx 4.9 \times 10^7$ cm⁻¹). The coulomb pseudo potential μ^* is calculated as 0.22 and is due to the fact that ϵ_F is higher at least an order of magnitude with ω_{er} .

The electron-phonon coupling strength λ using Eq. (10) is obtained as 1.8 for ω_{er} . In the regime $\lambda > 1$ the strong coupling theory applies and T_c for Rb_3C_{60} is given as

$$T_c^{er} = 0.25 \omega_{er} [\exp(2/\lambda_{eff}) - 1]^{-1/2} \quad (11)$$

Where

$$\lambda_{eff} = (\lambda - \mu^*) [1 + 2\mu^* + \lambda\mu^* t(\lambda)]^{-1} \quad (12)$$

Here λ_{eff} is the effective coupling constant and T_c^{er} is estimated as $\approx 8K$ which is much lower than the reported experimental data. Both intermolecular and intramolecular phonons in fullerenes the result [14] for T_c is given as

$$T_c = T_c^{er} [\omega_{ra} / T_c^{er}]^\eta \quad (13)$$

with

$$\eta = \lambda_{ra} / (\lambda_{ra} + \lambda_{er}) \quad (14)$$

λ_{ra} being the intramolecular coupling constant and is obtained as 0.7 . Using ω_{ra} from the reported data [1], T_c is obtained as $33 K$.

Isotope effect exponent

The isotope effect coefficient is

$$\alpha = (\omega/2T_c)(dT_c/d\omega) \quad (15)$$

Using the relation $d\mu^*/d\omega = \mu^*/2\omega$, α follows

$$\alpha = \{1 - \mu^{*2}[1 + 2\lambda + \lambda^2 t(\lambda)] / \lambda_{eff}(\lambda - \mu^*) [1 + (4T_c/\omega)^2]\} / 2 \quad (16)$$

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} (Rb) and a finite value of carbon isotope effect is calculated. Eq. (16) gives $\alpha = 0.45$ (0.39), which is consistent with the reported data. A shift in T_c is an indication of an important role of coupling of the conduction electrons [17] with the displacement of C_{60} molecule or alkali ions.

VI. CONCLUDING REMARKS

In the present approach the role of intermolecular and intramolecular phonons in pairing and anomalous carbon isotope exponent of Rb_3C_{60} is tried to trace within phonon mechanism. Treating the 3D Rb_3C_{60} as a diatomic lattice of Rb_3 and C_{60} the force constants and dispersion relations are obtained. T_c due to intermolecular phonons is first obtained as $8K$. Keeping in mind that intramolecular phonons do indeed play a significant role; an increase in T_c is predicted. The appropriateness of the proposed approach depends on proper consideration of structure for $8N C_{60} - K$ bonds out of which $4N$ are at octahedral position and $4N$ takes the tetrahedral sites.

Due to the simplicity of the approach, the calculated values of T_c and α are consistent with the reported data. The deduced value of coupling strength for the intermolecular phonons 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.

The intramolecular phonon pairing mechanism must be a viable mechanism for alkali metal intercalated fullerenes. Several recent 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 intermolecular and intramolecular phonons participate in the superconducting state as well as essential for superconducting fullerene properties as transition temperature and carbon isotope effect. Our results are of interest and provide a test of the possibility of cooperative mechanism in alkali metal fullerene superconductors.

The present analysis predicts a consistent value of transition temperature and reduced value isotope exponent α when comparison is made with BCS limit and favours strong coupling mechanism in Rb_3C_{60} . we found that superconductivity in fullerenes incorporates all three energy scales like Coulomb, electron – intermolecular phonons and electron – intramolecular phonons.

In the present study, it is clear that the basic theory of superconductor in fullerenes and some important properties of alkali metal intercalated fullerenes are well estimated. Unlike conventional superconductors, the main mechanism for fullerene superconductivity is related to both intramolecular and intermolecular properties. Intramolecular properties means the electron – phonon coupling strength and the intermolecular properties imply the density of state at the Fermi level. At large inter fullerene distance, alkali metal – C_{60} (A_3C_{60}) interactions are crucial leading to non rigid band behaviour, even though some structural transition occurs leading superconducting state.

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