

THEORIES OF SUPERCONDUCTIVITY IN ALKALI DOPED FULLERIDES¹

S. N. Behera²

Institute of Physics, Sachivalaya Marg,
Bhubaneswar-751005, INDIA.

Abstract A brief review is presented of the some of the essential features of fullerenes, fullerites and alkali doped fullerides. The review starts with a short account of the discovery of the fullerene and discusses some of the properties of the molecule. Some properties of the solid fullerites and their understanding in terms of the electronic structure is also presented. Emphasis is placed on alkali doped fullerides and the superconductivity in these systems. Experimental evidences indicating the possible mechanism for superconductivity and the present status of the theories of superconductivity in these systems are analysed.

Keywords : Fullerene, Alkali doped fullerides, Superconductivity.

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² e-mail: snb@iopb.ernet.in

1. Introduction

It was known for a long time that carbon exists in nature in two different forms namely graphite and diamond. Graphite has a layered structure in which each carbon atom has a three fold coordination. On the otherhand diamond, the hardest material on the earth ; has a three dimensional tetrahedral structure with the carbon atoms having four fold coordination. In 1985 a third form of carbon was discovered by Richard Smalley and Harold Kroto [1], which is a molecule of sixty carbon atoms (C_{60}). They called it the Fullerene or the Buckyball. However, the full impact of the dicoverery was realized only after Kratschmer and Huffmann [2] demonstrated in 1990 how Fullerene can be isolated in bulk form, which made it possible to study the properties of this new form of solid carbon. It was found that eventhough crystalline fullerene is an insulator, on doping it with alkali metal atoms it starts conducting and becomes a superconductor [3] at low temperatures. The transition temperatures (T_c) of these alkali doped fullerides are found to be rather high, e.g, $T_c = 19K$ for K_3C_{60} , $28K$ for Rb_3C_{60} and $33K$ for Cs_2RbC_{60} ; which qualifies these to be categorized as high T_c superconductors. In this review we shall discuss the nature of the superconducting state of the alkali doped fullerides as evidenced from various experimental results and briefly discuss the various theoretical proposals put forward to explain these observations. However, before discussing aspects of superconductivity we shall briefly summarize the properties of the fullerides and also present a brief history of the discovery of the fullerene, which by itself is very fascinating.

2. Discovery of Fullerenes : A brief History

The story of the search that led to the discovery of the C_{60} molecule is very exciting. Two groups were indepenently looking for linear chain molecules of carbon containing more than two carbon atoms for entirely different reasons. The motivation of the first group led by Harold Kroto of the University of Sussex, stemed from his interest in analyzing the contents of common soot, which he believed contained long chain carbon molecules of different

sizes. When he learnt that Richard Smalley of the University of Houston has built a cluster generator, with which these molecules can be produced, they decided to put their efforts together to produce these exotic carbon molecules. In a cluster generator a graphite sample is vapourized by hitting it with a powerful laser beam. The debris thus produced is collected

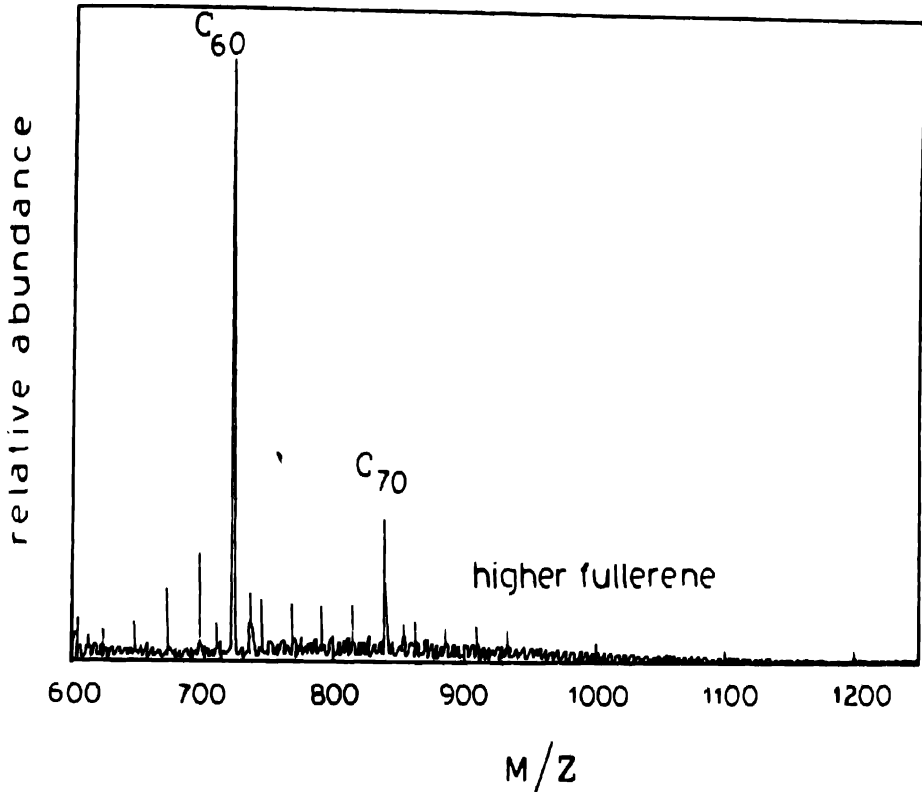


Fig.1. The mass spectrum of the carbon clusters. The strong peaks correspond to C_{60} and C_{70} (taken from C. M. Lieber and C. C. Chen in *Solid State Physics* Vol. 48 (Academic Press N.Y. 1994) Eds. H. Ehrenreich and F. Spaepen).

by allowing the flow of helium gas whose pressure can be controlled and optimized. Subsequently the helium gas carrying the carbon particles is passed through a nozzle and allowed to cool. The carbon clusters are formed when the gas cools, then the particle beam is mass analyzed by passing it through a mass spectrometer. The mass spectrum showed a very

strong peak (Fig.1.) at a mass corresponding to sixty carbon atoms ; and another smaller peak at seventy carbon atoms ; which clearly exhibited the relative stability of clusters of sixty carbon atoms. In order to determine the structure of this cluster of sixty carbon atoms

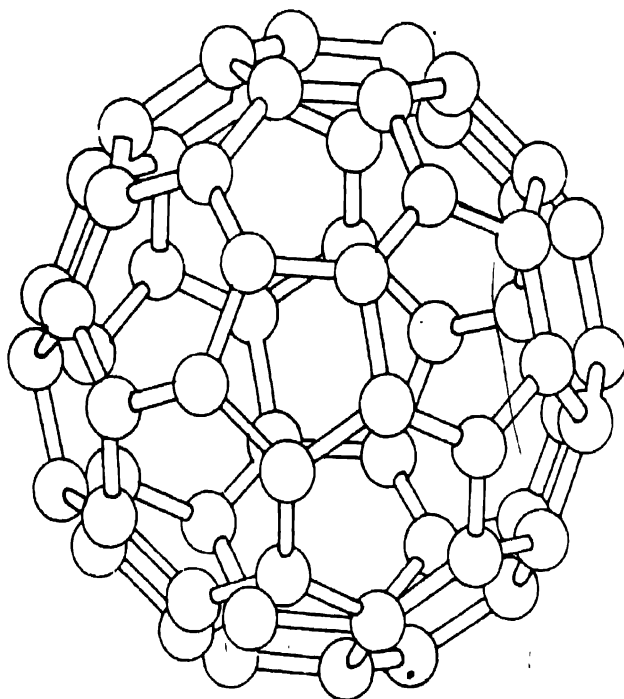


Fig.2. The foot ball structure of the fullerene molecule containing 12 pentagons and 20 hexagons with the carbon atoms attached to the corners of the pentagons.

their nuclear magnetic resonance (NMR) spectrum was investigated, which showed a single peak. This clearly demonstrated that all the carbon atoms in the cluster occupy equivalent positions, hence the structure must be highly symmetrical like a sphere. Naturally, it led to the question of how to wrap a graphite sheet into a sphere? However, since graphite sheets consists of a network of hexagons, it was soon realized that it is imposible to form a sphere out of it. But the sheet can be curved by adding pentagons to the hexagonal network and one can proude a spherical structure like that of a football, with 12 pentagons and 20 hexagons. Thus the structure of the C_{60} cluster is determined, the carbon atoms occupy the

corners of the pentagons, with the single bonds shared between pentagons and hexagons, while a double bond links two adjacent hexagons. Thus there are sixty single bonds and thirty double bonds which accounts for the 240 valence electrons of the sixty carbon atoms. This structure of the C_{60} molecule is shown in Fig.2. This molecule is named the Fullerene or the Bucky ball in honour of the American architect Buckminster Fuller, who had studied extensively the stability of structures and established that a geodesic structure is the most stable one. Thus the discovery of the fullerene was announced in 1985 by Smalley and Kroto.

In contrast the other group who were looking for long chain carbon molecules were led by W. Krätschmer of the Max Planck Institute of Nuclear Physics at Heidelberg and Donald R. Huffman of the University of Arizona at Tucson both of them sharing an interest in astrophysics [4]. Their primary interest was in identifying the atoms and molecules present in the interstellar space, by examining the optical absorption spectrum due to the interstellar dust. In this spectrum there appears a band of lines between the energies of 1.6 and 2.8 eV which remained unidentified and there was a hunch that these lines may be associated with the presence of long chain carbon molecules in interstellar space. Hence their main interest was to make these molecules in the laboratory so that their optical spectrum can be studied. The device used by them to produce these molecules essentially consisted of a graphite electrical arc, which when struck in an inert gas (Helium) atmosphere produced soot which can be collected and analyzed. The soot was collected under conditions of different pressures of the helium gas, and the optical absorption spectrum of these samples were studied both in the ultraviolet and the infrared regions. Some of these samples showed a double peaked structure in the ultraviolet (see Fig.3.) which could not be identified. This spectrum was nicknamed the camel back spectrum. The infrared spectrum of the same camel back samples showed four different peaks which again could not be identified with any known carbon molecule (see Fig.4.). It is only after the announcement of the discovery of fullerene, that its ultraviolet and infrared spectra are found to be identical to those of the camel back samples of Krätschmer and Huffman. They thus missed the opportunity of being the discoverers of fullerene. However their efforts did not go waste. They were the first to succeed in producing the fullerene samples in the bulk quantity after a couple of years of its discovery. Eventhough

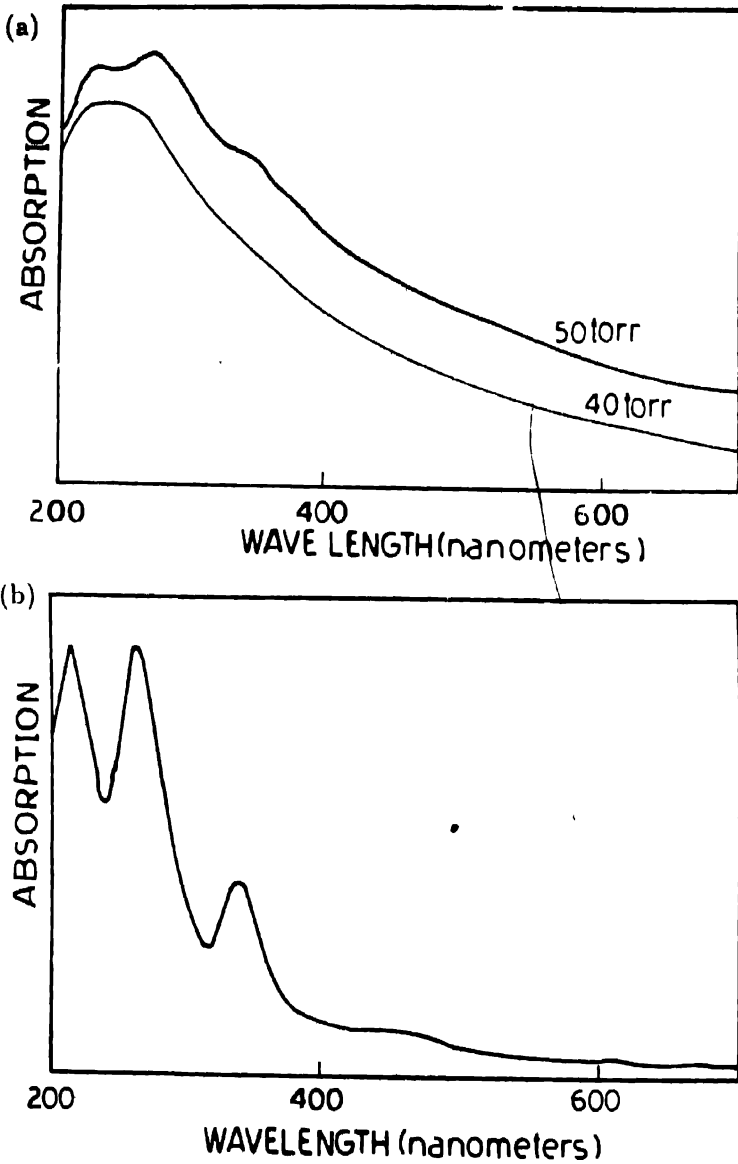


Fig.3.(a) Ultraviolet spectra of the graphite soot containing C_{60} (upper curve) and graphitic soot without C_{60} (lower curve). (b) U-V spectra obtained by subtracting lower curve from the upper one in (a) (taken from [2]).

the fullerene molecule was discovered, it was not possible to isolate these molecules in a bulk

form. Hence all the measurements of their properties had to be carried out in situ inside the cluster generator as they are being produced. Or else these properties had to be carefully

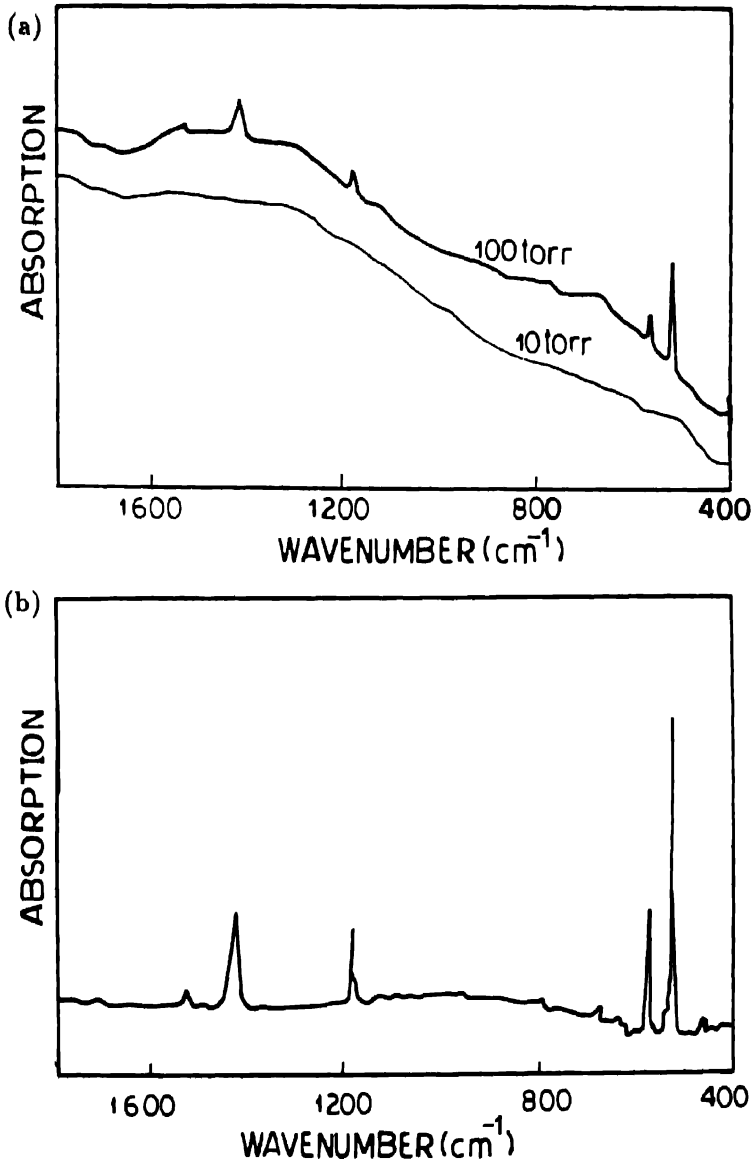


Fig.4. (a) Infrared spectra of the same two samples as in Fig.3. (b) Spectra obtained by subtracting the lower curve from the upper one. Notice four distinct infrared lines which characterize the C_{60} molecule. (taken from [2])

identified by performing measurements with the soot which contained fullerenes along with a lot of debris ; which was a pains-taking and difficult process. Therefore not much progress could be made in the study of the properties of the fullerenes, in the absence of a process to isolate it in bulk quantities. For the first time in 1990, Krätschmer and Huffman [1] found a way of isolating fullerenes in solid form, with which the fullerene research gained tremendous momentum. The process was based on what is known as a simple thumb rule in chemistry, i.e, solvents of like molecules dissolve similar solutes. Since fullerene molecules have a closed structure it is likely that it will be dissolved in liquid benzene the molecules of which also have a closed ring structure. With this in mind they tried to dissolve their camel back sample of the soot which contained the C_{60} and C_{70} molecules in benzene liquid. On thoroughly mixing the soot in benzene, it was found that the colour of the liquid changed to orange-red, indicating that some portions of the soot has indeed been dissolved in the liquid. Then the clear liquid was poured out into a beaker and heated to evaporate the benzene. The residue that was left behind contained a mixture of C_{60} and C_{70} . Thus the solid fullerite was isolated. It can also be crystallized by following the same process. This discovery opened up the flood gates for the study of the properties of solid fullerene.

3. Properties of Fullerene

The spherical fullerene molecule has sixty single and thirty double bonds. The bond lengths compare well with those of the other forms of carbon, e.g, the length of the single bond in the three fold coordinated graphite is 1.42 \AA , and that in four fold coordinated diamond is 1.54 \AA , while in fullerene it has a value in between being 1.455 \AA . Similarly the length of the short bond for C_{60} is 1.391 \AA . The diameter of the fullerene cage is 7.1 \AA , which is rather large compared to other atoms and molecules. The interior of this huge spherical molecule is almost empty with all the electron density accumulated on the surface of the sphere [5]. Thus it acts as a perfect trap of other atoms and ions which can be encapsulated inside this molecule. Studying the properties of such trapped atoms and

Table 1. Properties of Solid C_{60} .

1. Density	1.65gms/cm ³
2. Index of refraction at $\lambda = 630\text{nm}$ s	2.2
3. Bulk modulus	18 Giga Pascals.
4. Ionization Potential of C_{60} molecule	7.6 ev
5. Electron Aafinity of C_{60} molecule	2.6 – 2.8 ev
6.(a) Cohesive energy : per molecule	1.5 ev
6. (b) Cohesive energy : per atom	7.4 ev.
7. Band gap energy	1.9 ev.
8. Infrared active modes.	1429, 1183, 577, 528cm ⁻¹ .
9. Raman frequencies	272, 429, 495, 711, 772, 1099, 1250, 1422, 1467, 1573 cm ⁻¹
10. Libration frequency (5K)	22cm ⁻¹

molecules in itself has immense potentialities so far as basic research is concerned. The C_{60} molecules crystallise with the face centred cubic (fcc) crystal structure, in which the molecules are very loosely bound, the cohesive energy per molecule being 1.5 ev. In contrast the carbon atoms in the molecule are rather strongly bound ; with the cohesive energy per atom taking the value of 7.4 ev. The lattice constant of the crystal is very large, i.e, 14.198 Å , while the nearest neighbour distance is 10.04 Å . Thus in the solid the closest approach between two C_{60} molecules is 3.1 Å . These numbers have to be contrasted with those of the elemental solids such as a metal, in which case the typical lattice constants are of the order of 3 – 4 Å . So far as the electrical properties are concerned, pristine C_{60} solid is an insulator, with a band gap of 1.9 ev. This value of the band gap is in keeping with the expectations from the optical properties of the fullerene. For example the orange - red colour of fullerene dissolved benzene, itself suggests a band gap of the order of 2.2 evs. Some of the other properties of C_{60} solid are given in table 1. [6].

The electrical properties of the fullerenes can be understood in terms of the electronic

structure of the fullerene molecule. The molecule has 60 atoms, which contribute 240 valance electrons. But out of the four valance electrons per carbon atom three go to the bonding orbitals and only one electron per atom is left free in the p_z or π -orbital which can contribute to the electrical properties of the solid. Thus there are 60 electrons which move on the surface of the sphere of the soccer ball structure in the periodic potential provided by the sixty carbon atoms of the fullerene molecule. In a simplified approach to the electronic structure of the fullerene molecule one can think of these electrons as moving on the surface of a sphere. Thus the motion of an electron is that of a rigid rotator, so that the energy eigen values are proportional to $l(l+1)$, l being the orbital angular momentum which takes integral values. The eigen value corresponding to the quantum number l is $(2l+1)$ fold degenerate. Thus the lowest $l=0$ s-level can accomodate 2 electrons, the p -level being three fold degenerate can accomodate 6 electrons, the d with $l=2$, 10 electrons and so on. Hence out of the sixty π -electrons 50 electrons can fill up all the leveles upto the $l=4$ the g -level, leaving the 11 fold degenerate $l=5$ level only partially occupied with 10 electrons. In which case the simple spherical model predicts solid C_{60} to be a metal. However, on accounting for the lowering of the symmetry from the spherical one, due to the truncated icosahedron structure of the molecule, the degeneracy of some of the levels will be lifted. For example, the $l=5$ level splits into a five fold degenerate h_u level and two three fold degenerate t_{1u} and t_{2u} levels. The lowest five fold degenerate h_u level gets fully occupied with the 10 remaining electrons and the solid turns out to be an insulator. The electronic states thus generated can be enumerated by a simple Hückel type molecular orbital calculation. The energy levels corresponding to these states are shown on the left side of Fig. 5., which are labelled according to the symmetry classification as a , t , g and h each having a degeneracy of one, three, four and five respectively. Since each state can accomodate two electrons, the sixty free electrons of the molecule occupy up to the level denoted h_u ; which is therefore the highest occupied molecular orbital (HOMO). The level t_{1u} which is three fold degenerate is just above the HOMO and is the lowest unoccupied molecular orbital (LUMO). It is worth noting that the LUMO level is close to the zero of energy, therefore the electron affinity of the fullerene molecule is expected to be rather high, which is in confirmity with the measured

value. On forming a solid each of these energy levels corresponding to the molecular orbitals

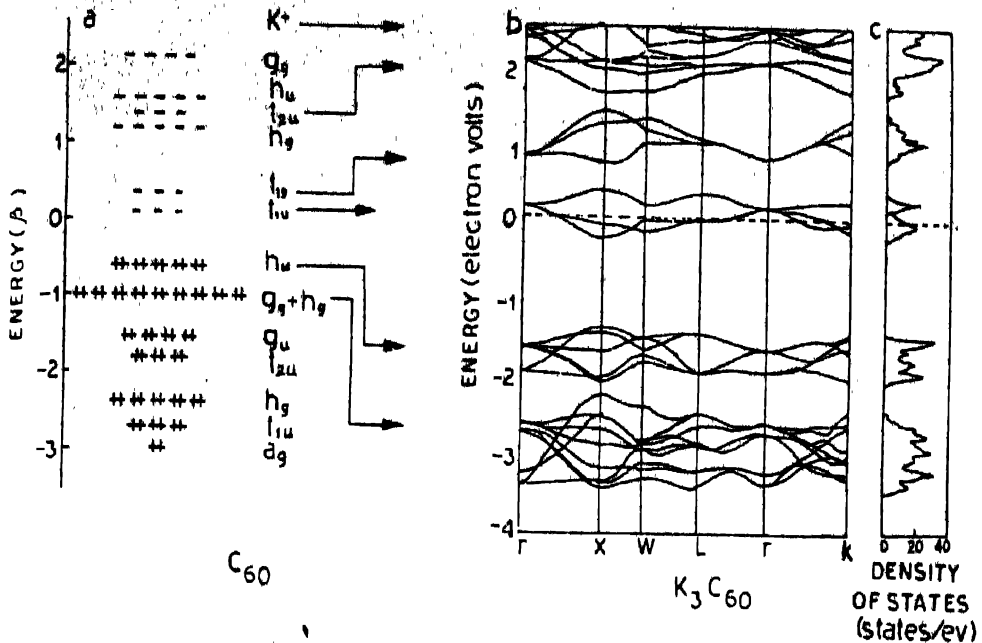


Fig.5.(a) Electron energy spectrum of the fullerene molecule obtained from a Hückel type calculation. The labels a, t, g and h have degeneracies of 1, 3, 4 and 5 respectively. (b) The calculated band structure for K_3C_{60} in the local density approximation (LDA). The Fermi level is shown by the dashed line. (c) The density of states for the bands showing the peaked structure. Note the Fermi level lies close to one of the peaks in the LUMO band (taken from [5]).

will spread into a band, as per the expectations from the tight binding picture of the band theory. However, the lattice constant of the solid C₆₀ being very large the band widths are expected to be smaller compared to the conventional solids. Furthermore since some of the molecular orbitals have rather high degeneracies and all the bands are narrow; the density of states is expected to be very large. The band structure of solid C₆₀ as calculated from the local density approximation (LDA) [7] is shown on the right side of Fig.5. Clearly the calculation shows a band gap of around 1.5 eV, which is again very close to the experimental value. Thus the band structure calculation predicts that solid C₆₀ will be an insulator. As

expected the widths of the valance and conduction bands are narrow being about 0.5eV. The density of electronic states as determined from this band structure calculation is shown further to the right of Fig.5., which clearly shows large values of the density of states.

Another interesting feature of the fullerides is that it is a disordered solid at room temperature. In the solid the fullerene molecules execute free rotation at room temperature. There are two distinctly different axes around which this rotation can take place ; namely an axis passing through the center of a pentagon or an axis passing through the centre of a hexagon. On lowering the temperature or doping the solid with other atoms and molecules the rotations are hindered and may stop ; in which case the solid can still be in a disordered state with the individual molecules randomly oriented along one or the other axis. On further lowering the temperature the fulleride can undergo a transition to an ordered state. Such order-disorder transition have been observed in C_{60} solid [8]. The electronic states can also be effected by such order-disorder transitions.

4. Alkali Doped Fullerides

The C_{60} molecules in the solid are very loosely bound, consequently there is a lot of space available into which other atoms and molecules can be intercalated. In fact the fcc unit cell can accomodate six such atoms in the tetrahedral and octahedral sites. It was found that alkali atoms can be easily doped into the fullerene solid. However the solid solution A_xC_{60} (where A is an alkali atom like K , Rb , Cs) is found to have a stable structure only for $x = 3$ and 6. While with three alkali atoms per unit cell the structure still remains fcc, it changes to the bcc structure when the number of atoms increases to six per unit cell [5]. The electrical properties of the pristine fulleride changes drastically with increasing number of the dopant alkali atoms ; from being an insulator to a metal for A_3C_{60} and again an insulator for A_6C_{60} . This behaviour can again be understood in terms of the electronic structure of the solid fullerene depicted in Fig. 5. The alkali atoms in the doped system essentially acts as electron donors, with the valance electrons occupying states in the empty conduction band formed out of the t_{1u} orbitals, which are three fold degenerate. Therefore

in the case of the solid solution A_3C_{60} , the three valance electrons of the of the alkali atoms occupy the LUMO state of C_{60} molecule, consequently the conduction band of the C_{60} solid gets exactly half-filled turning it into a metal. On the otherhand, for A_6C_{60} the conduction band is completely filled up and since the next unoccupied band is separated by a gap (see Fig. 5.) the solid solution turns out to be an insulator. It is worth noting from Fig.5. that in case of A_3C_{60} the Fermi level falls just above a peak in the density of states, with $N(\epsilon_F)$ taking a rather high value of about 20 states/ev.

As mentioned in the introduction the metal A_3C_{60} becomes a superconductor at low temperatures. The transition temperatures and some of the other properties related to superconductivity of the alkali doped fullerides are listed in table 2. [9].

5. Theories of Superconductivity in the Doped Fullerides

The superconducting transition temperature (T_c) of the alkali metal doped fullerides are comparatively much higher than the conventional low temperature superconductors. Because of this sometimes these are classified as high temperature superconductors along with the oxide superconductors [10]. However if one uses the Batalog plot (which plots the transition temperature as a function of Sommerfield coefficient or the density of states at the fermi level) as a criterion for distinguishing between the high and low temperature superconductors, the fullerene superconductors fall just below the line of demarkation. Since the density of state at the fermi level for the alkali doped fullerides is rather high (Sec. 4.) the T_c 's are not large enough for these to belong to the category of the high temperature superconductors. But this is a crude classification based on the systematics of all the known superconductors, and if one takes this criterion seriously then it is expected that the meshanism of superconductivity in these systems can be understood in terms of the BCS theory [11]. However right after the discovery of superconductivity in the alkali doped fullerides doubts have been raised regarding the validity of the BCS theory as applied to these systems [12] and alternatively purely electronic mechanisms have been proposed. In what follows we shall examine the experimental evidence in suport of either of these mechanisms and discuss the pros

Table 2. Properties of Alkali doped A_3C_{60} fullerides.

1. Crystal structure	<i>Cubic</i>
2. Effective mass of carriers	$1.3 m_e$
3. Nature of superconductivity	Type II
4. Transition temperature of (T_c) K_3C_{60}	19K
Rb_3C_{60}	28K
Cs_2RbC_{60}	33K
5. Pressure dependence of $T_c : \frac{\delta T_c}{\delta P}$	-0.63 to -0.78K/kbar.
6. Lower critical field : $H_{c1}(0)$	0.013 T.
7. Upper critical field : $H_{c2}(0)$	49 T.
8. Coherence length ξ	26 Å°
9. Penetration depth $\lambda(0)$	4800 Å°
10. NMR Chemical shift	186 ppm
11. Ginzburg-Landau parameter $K(\lambda_L/\xi)$	
K_3C_{60}	92
Rb_3C_{60}	124
12. $2\Delta/k_B T_c$	5.2

and cons of these theories. Till to-date there is no general concensus regarding the theory of superconductivity in the alkali doped fullerenes and the problem still remains an open one.

5.1 Phonon Mechanism and the BCS theory

It is well known that in the BCS theory, there is pairing of two electrons in the zero momentum singlet state (cooper pairs) due to an attractive interaction mediated by the phonons. The direct experimental evidence which pointed towards the phonon mechanism came from the measurement of the isotope effect. In the weak coupling limit the transition temperature in this theory is given by,

$$T_c = 1.14\omega_D \exp[-1/N(0)V] \quad (1)$$

where ω_D is the frequency for the phonon, $N(0)$ is the electronic density of state at the fermi level and V is the effective coupling constant due to the phonon mediated interaction. Furthermore the quasiparticle energy in the superconducting state is given by,

$$E(k) = [\epsilon^2(k) + \Delta^2]^{1/2} \quad (2)$$

where $\epsilon(k)$ is the energy of the free electron and Δ is the superconducting gap parameter. Thus the energy spectrum has a gap of 2Δ at the Fermi level. One of the predictions of the BCS theory is that the ratio of the gap to the transition temperature ($2\Delta/K_B T_c$) = 3.5. Eventhough the measured value for most of the conventional superconductors agree with this prediction, there are deviations in a few cases. This called for an improvement of the theory so that cases of strong coupling between the electrons and the phonons can be accounted for properly. In the BCS theory this coupling is assumed to be weak which allows for the elimination of the phonon degree of freedom in favour of an effective interaction between the electrons. Therefore in the weak coupling theory the phonons do not play any role in the dynamics of the superconductor except for providing an energy cut-off (eqn.(1)). However, this picture will break down if the electron-phonon interaction is strong, which requires the explicit consideration of the phonon degrees of freedom in the dynamics of the system. Such

a strong coupling theory was developed by Eliashberg [13], which was quite successful in explaining the deviations of the properties of some superconductors from BCS theory. The strong coupling theory also puts a limit to the highest T_c achievable by the phonon mediated pairing. It follows from eqn.(1) that in the weak coupling theory, the T_c can be increased to any value by increasing either the phonon frequency ω_D or the density of states $N(0)$ or the coupling constant V or all these quantities simultaneously. Besides the effect of the coulomb repulsion between the electrons does not enter this weak coupling formula for T_c . But the strong coupling theory predicts that it is not possible to increase T_c by increasing these quantities simply because increasing the phonon frequency decreases the strength of interaction and an unusual increase in the coupling constant will produce a lattice instability. Similarly increasing the density of states will also increase the coulomb repulsion which is not conducive to superconductivity. Thus the strong coupling theory sets a limit of about 40K for the highest achievable T_c by the phonon mediated pairing. Furthermore this theory also accounts for higher values of the ratio $2\Delta/K_B T_c > 3.5$, thus explaining the deviations observed in some of the conventional low temperature superconductors.

5.2 Experimental Indications for the phonon mechanism

We shall now analyse the evidences for the applicability of phonon mediated pairing and the BCS theory to superconductivity in alkali doped fullerenes. In these systems even though the transition temperatures are high they are still within the limits set by the strong coupling theory. Therefore one would like to examine if there is any direct experimental evidence for phonon mediated pairing and also for the strong coupling between the electrons and phonons. It was already pointed out in sec.4. that in the alkali doped fullerenes the density of states at the fermi level is rather high, which will probably account for the high T_c in these systems, within the frame-work of the BCS theory. Furthermore as can be seen from table 2. the T_c increases with increasing ionic radii of the dopant alkali atoms i.e. on going from K to Rb to Cs. This is equivalent to applying larger internal negative pressure, which will result in an increase in the lattice constant. On the otherhand these systems have

a large negative pressure derivative of the transition temperature (see table 2.). Application of pressure causes a lattice contraction. The overall pressure dependence of T_c is shown in Fig.6., [4] from which it can be deduced that T_c has almost a linear dependence on lattice constant.

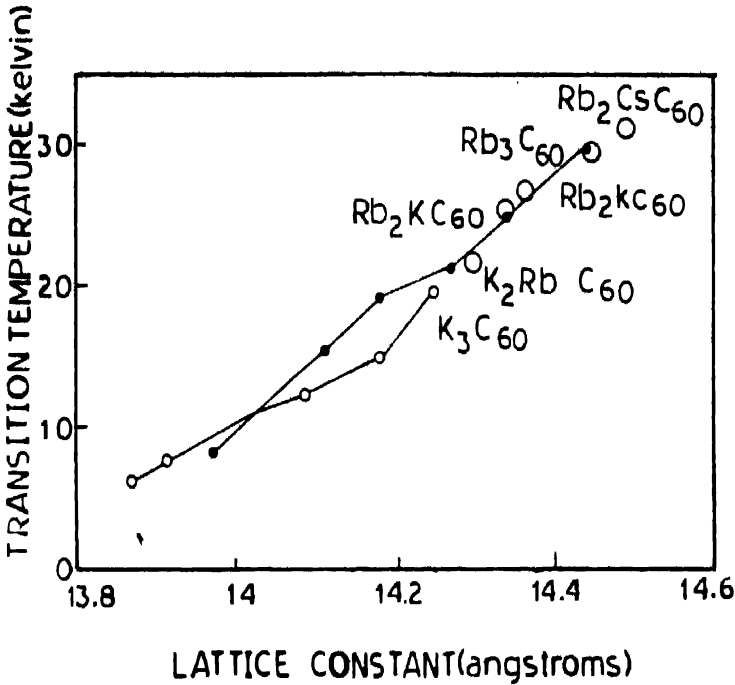


Fig.6. The superconducting transition temperature (T_c) as a function of the lattice constant, whose values are extracted from measurements carried out by applying pressure and also by doping the solid with a mixture of alkali atoms of different atomic radii (taken from [5]).

This again can be understood qualitatively as a density of states effect ; i.e with decreasing lattice constant the band widens and hence the density of states decreases. This explains why with increasing pressure the T_c decreases. On the other hand doping the system with alkali atoms of large atomic radii increases the lattice constant, consequently the bands become narrower thus increasing $N(\epsilon_F)$ and consequently the T_c . But probably the most direct evidence for the involvement of phonons in the mechanism of superconductivity and hence the validity of the BCS theory again comes from the isotope effect [15] as shown in Fig.7. It

is replacing an atom by its heavier isotope in the superconductor the transition temperature increases. The dependence of T_c on the mass of the atom is given by $T_c \propto M^{-\alpha}$, with $\alpha = 0.5$ for most of the conventional superconductors.

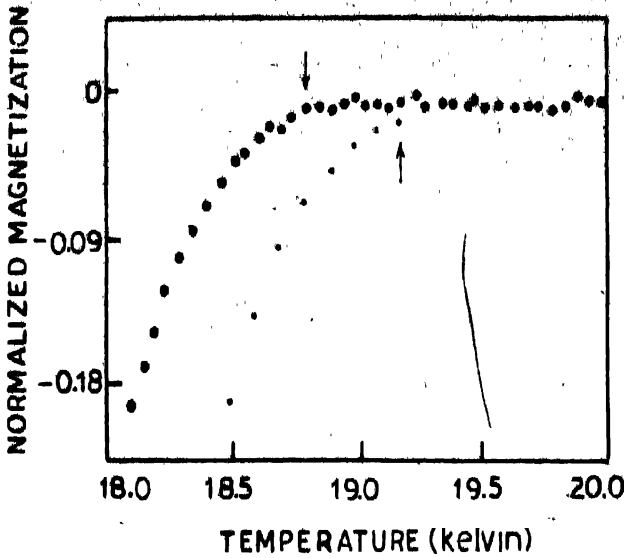


Fig.7.. Isotope shift of the transition temperature for $K_3^{13}C_{60}$ as compared to $K_3^{12}C_{60}$. The transition temperatures as obtained from the magnetization transition are marked by arrows (taken from [8]).

It can be seen from the figure that T_c for the isotopically pure $K_3^{13}C_{60}$ occurs at a temperature 0.4K lower than that for $K_3^{12}C_{60}$, which is a clear cut indication of an isotope shift. However the measured shift is lower than that of the calculated value $\delta T_c = -(1/2)(\frac{\delta M}{M})T_c = -0.8K$, by a factor of 2, which is a deviation from the predictions of the BCS theory. Moreover it should be pointed out that the measured values of the isotope exponent α varied widely, e.g, in the case of the Rb doped fullerides α values ranged between 0.4 to 2.0. This puzzling feature was further clarified through a clever experiment by Chen and Lieber [16], who repeated their earlier measurement [15] with two distinct substitutions of 50% ^{13}C . In one case, each C_{60} molecule had $\sim 50\%$ of each isotope, while in the other case each molecule

was entirely composed of either ^{13}C or the ^{12}C isotopes, but the solid was made out of 50% mixture of the molecules of different masses. Different shifts of T_c was observed in the two cases. For the homogeneous case where all the molecules have both isotopes, α was found to be 0.3 in agreement with their earlier measurement, whereas in the inhomogeneous case, with each molecule consisting of one isotope only, the shift in T_c was anomalously large. This experiment also provided evidence in support of the intermolecular modes being strongly involved in the phenomenon of superconductivity. But all the same these measurements points towards the phonon mechanism of superconductivity

5.3 Phonons in the Alkali doped Fullerenes

The next question that one would like to ask is which phonon and how strong is its coupling with the electrons. Some indication regarding the nature of the electron phonon interaction in the alkali doped fullerenes comes from the Raman measurements. It is well known that Raman Scattering is essentially inelastic scattering of light, where the scattering takes place by exciting (stokes) or absorbing (antistokes) the zone centre (i.e the zero wave vector $q = 0$) optic phonons of the crystal. The Raman spectra of pristine and alkali doped fullerenes are shown in Fig.8 [17]. In the pristine C_{60} solid a large number of phonons are clearly visible (Fig. 8a) in the Raman spectrum. However, the spectrum changes drastically in the case of the A_3C_{60} ($\text{A} = \text{K}, \text{Rb}$) samples as can be seen from Fig.8(b). Most of the phonons are totally suppressed with only three or four being detected by the Raman scattering. On changing the composition of the alkali doped fullerenes to A_6C_{60} ($\text{A} = \text{K}, \text{Rb}, \text{Cs}$) the suppressed phonons reappear in the Raman spectrum. The pristine and the A_6C_{60} samples are insulators while the A_3C_{60} samples are metallic in character. Therefore, the disappearance of phonons from the Raman spectrum of the A_3C_{60} samples can be attributed to the interaction of these with the free charge carriers in these systems. It can be argued that because of strong electron phonon interaction the line widths of the phonons increases so much that their intensities in the Raman spectra gets reduced. Thus it can be inferred from the Raman data that in the metallic state of the alkali doped fullerenes the electron-phonon

coupling is rather strong. A closer examination of the Raman spectra of A_3C_{60} further reveals that it is the intramolecular H_g modes whose intensities are predominantly suppressed.

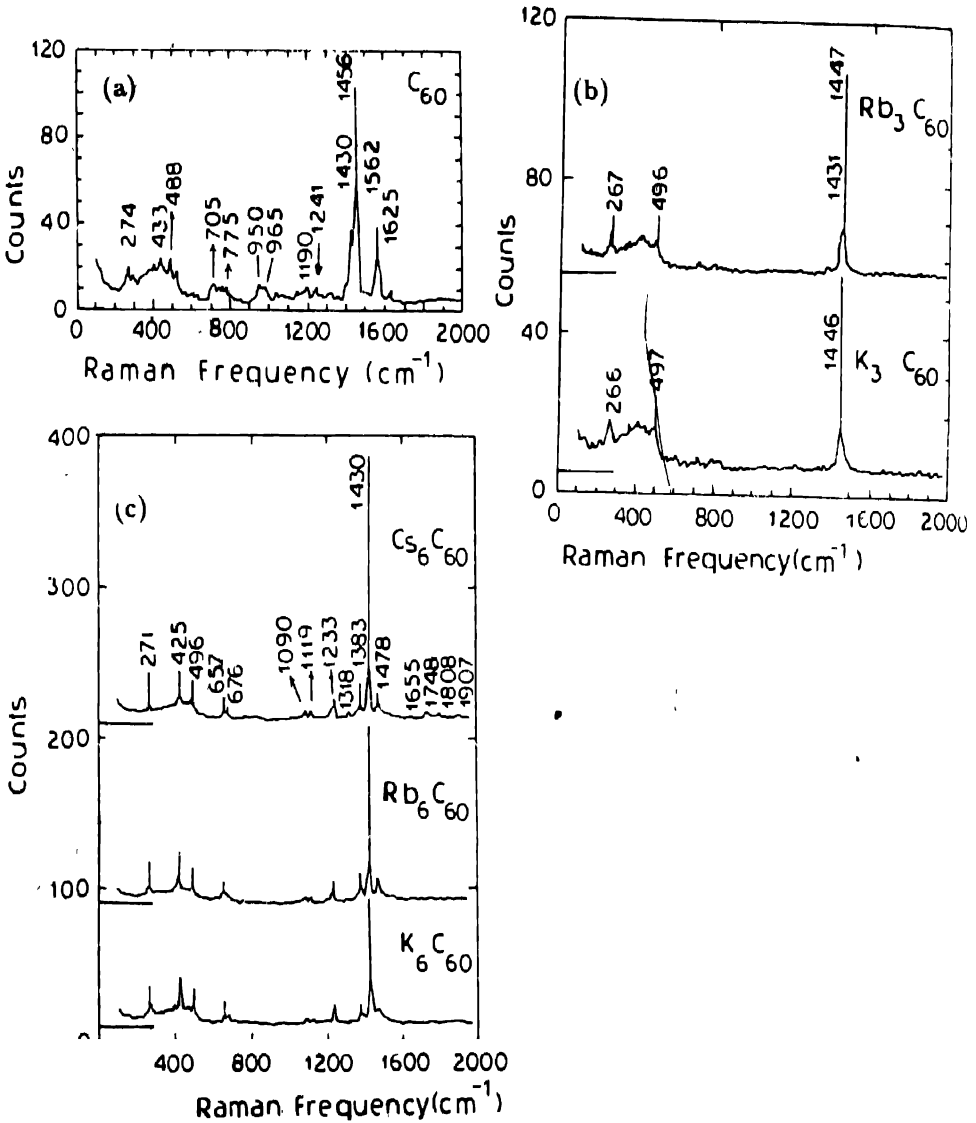


Fig.8. Raman spectra of (a) pristine C_{60} solid showing many phonons (b) that of the alkali doped fullerides A_3C_{60} (A = K, Rb) where suppression of the intensity of most of the phonons is noticeable, and (c) the Raman spectra of the alkali doped fullerides A_6C_{60} (A=K, Rb and Cs) where most of the phonons seen in the pristine sample reappear (taken from [17]).

Since only the zone centre phonons are involved in the light scattering process it can be further argued that the self-energy of these phonons due to electron-phonon interaction vanishes ; if the ground state of the system is a normal Fermi liquid like metal. Therefore a critical analysis of the Raman data suggests a non-Fermi liquid ground state for the A_3C_{60} systems. Assuming a fluctuating charge density wave ground state, the calculated Raman intensities, qualitatively show the suppression of intensity of some of the phonons [18].

The phonons observed in the Raman spectra of the C_{60} and A_xC_{60} solids have been identified. In fact a variety of vibrational modes are possible in C_{60} and A_xC_{60} solids [4]. First of all there exists the librational modes of the C_{60} molecules with very low frequencies in the range of $10 - 20\text{cm}^{-1}$. Since the solid has an fcc structure there is more than one fullerene molecule per unit cell, which allows for optic like out of phase vibrations of these molecules. Again the frequencies of these intermolecular vibrations are going to be very small because of the large mass of the molecule and the probable small force constants as indicated by the large lattice constant. Thus these frequencies will lie in the range of 20 to 50cm^{-1} . In the alkali doped fullerenes there is yet another possible optic mode arising from the out of phase vibrations of a fullerene molecule and an alkali atom within the same unit cell. The frequencies of these modes are going to be higher and can lie in the range of $50 - 100\text{cm}^{-1}$. However, the most dominant high frequency vibrations are those of the intramolecular kind where the carbon atoms within the fullerene molecule execute the vibrations. The frequencies of these vibrations span the range of 200 to 2000cm^{-1} . Out of these intramolecular modes the ones in which the carbon atoms on the ball move radially during the vibration, e.g, the symmetric breathing modes, do not involve the stretching of the carbon bonds and hence are the comparatively low frequency modes. On the otherhand the modes, in which the carbon atoms on the ball move tangentially on the surface of the sphere, will tend to stretch the carbon bonds, (e.g, as in the pentagonal pinch mode) ; and these require higher energies. Therefore the intramolecular modes with tangential on ball motion of the carbon atoms have rather high frequencies of the order of 1000cm^{-1} . Of all the observed Raman modes, the two with A_g symmetry having frequencies of 1458cm^{-1} and 488cm^{-1} in the case of the C_{60} solid have in fact been identified as the pentagonal pinch mode and the symmetric breathing mode respectively. All the other modes in the Raman spectrum with H_g symmetry are also intramolecular modes. The

various kinds of vibrational modes and their frequency ranges are depicted schematically in Fig.9. [4]. For the sake of clarity the pentagonal pinch mode is shown separately in Fig.10. It can be seen from Fig.8. that the frequency of this mode shifts to lower values with increasing dopant concentration as one goes from the pristine C_{60} (1458 cm^{-1}) to the alkali doped metallic A_3C_{60} (1445 cm^{-1}) to the insulating A_6C_{60} (1430 cm^{-1}). This softening of the pentagonal pinch mode can be attributed to the transfer of charge from the alkali atoms to the fullerene molecule.

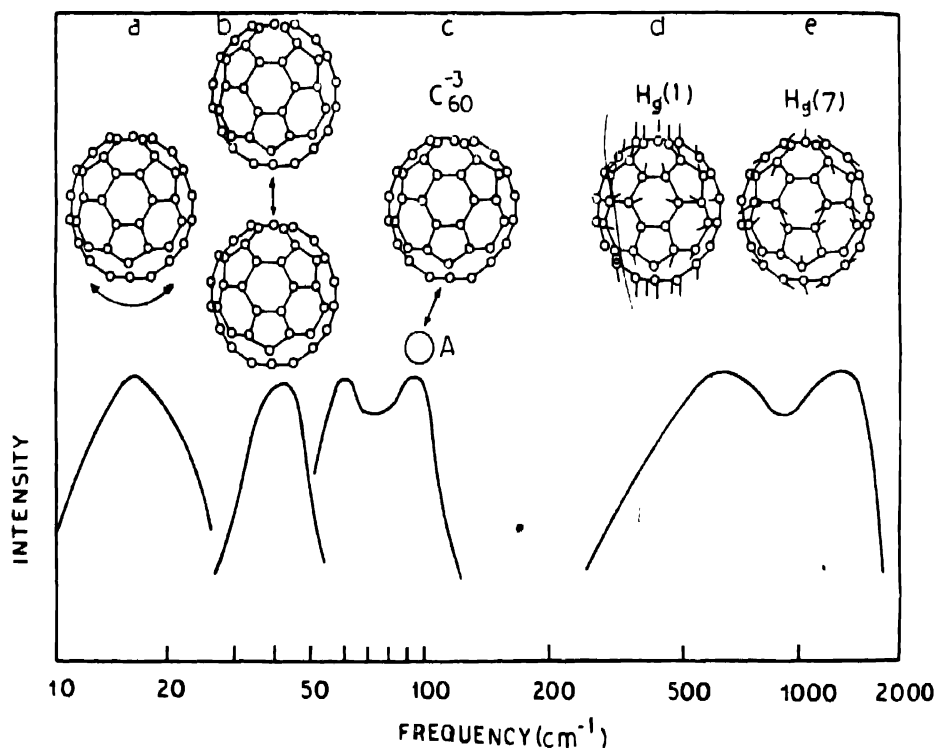


Fig.9. Schematic representation of various modes of vibrations and their frequency ranges of the alkali doped fullerides ; (a) The librational mode of the fullerene molecule. (b) The optic modes of vibration of the molecules in the unit cell. (c) The optic modes where the fullerene molecules execute out of phase vibrations against the alkali atoms in the unit cell. (d) The radial intramolecular vibrations of the carbon atoms in the fullerene molecule and (e) the tangential vibrations of the carbon atoms (taken from [5]).

The valance electrons of the alkali atoms are naturally transferred to the antibonding orbital of the

fullerene molecule. It is well known that occupation of the antibonding orbital increases the energy of the molecule, which in turn will result in an increase in the length of the carbon bonds. This will result in a decrease in the force constant and hence a softening of the phonon frequency. Thus

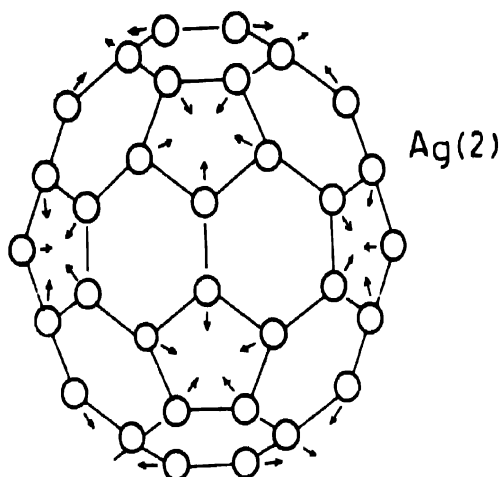


Fig.10. The intramolecular tangential $A_g(2)$ mode of vibration of the carbon atoms within the fullerene molecule. This mode has the high frequency of 1458 cm^{-1} in the pristine C_{60} solid.

the Raman measurements also provide the direct evidence for the charge transfer from the alkali atoms to the fullerene molecules in the doped fullerides. In fact from the measured frequency shift of the $A_g(2)$ phonon in a doped fulleride one can effectively estimate the amount of charge transfer from the dopant atom/molecule to the fullerene molecule. Furthermore the width of this mode decreases, the full width at half maximum (FWHM) being 15 cm^{-1} in the pristine C_{60} , 9 cm^{-1} in A_3C_{60} and 7 cm^{-1} in A_6C_{60} . The large width of the mode in the pristine sample can be attributed to the rotation-vibration coupling, because the C_{60} molecules are almost freely rotating at room temperature. On doping the sample with alkali atoms the free rotation of the C_{60} molecule is hindered and the libration is completely frozen in the A_6C_{60} samples at room temperature, thus reducing the rotation - vibration coupling strength of the pinch mode, which results in the narrowing of this mode.

5.4 Theories involving the Phonon Mechanisms

Several theories have been proposed for superconductivity in alkali doped fullerides invoking the

electron - phonon interaction as the mechanism for pairing. These theories give different weights to different phonons of the A_3C_{60} solid, the general trend being if low frequency phonons are involved then the coupling constant (λ) must be large, on the otherhand with the high frequency phonons λ must be small so as to reproduce the observed transition temperature. Varma et. al, [19] have argued that the high frequency intramolecular vibrations couple strongly to the electrons near the Fermi surface in the doped fullerenes and are responsible for superconductivity. Their calculation predicts that because of this interaction the high frequency on-ball modes in the SC samples will soften by about 5% and acquire widths of about 20% of their frequency compared to their values in insulating fullerenes. While the behaviour of the pinch mode presented in the preceding discussion of the Raman measurements seems to disagree with this prediction (the frequency softens but the width also decreases) ; the vanishing of the most of the H_g modes in the A_3C_{60} can be taken to be evidence in favour of this mechanism. On the otherhand Zhang et. al, [20] argue that the alkali ion - optic mode couples strongly with electrons, and therefore it is the low frequency phonons which are responsible for superconductivity. However, in this situation there will be a tendency towards a charge density wave (CDW) instability for the system, but it is argued that the fcc lattice of alkali doped fullerenes frustrates the CDW state and paves way for the SC state. There is also a calculation by Schluter et. al, [21], who computed the electron - phonon interaction strengths for all the phonons and showed that both the low and high frequency phonons will contribute to the coupling constants. Therefore the interaction of the electrons with all the phonons in the system is responsible for superconductivity. All these calculations use the strong coupling theory to estimate the critical temperatures. Assuming that the long range repulsive Coulomb interaction is properly screened as in conventional low temperature superconductors, the calculated T_c 's agree with the experimentally observed ones. The theory also reproduces the observed linear dependence of the T_c on the lattice constant.

5.5 Critic of the Phonon Mechanism

The strong coupling theory of superconductivity due to the phonon mechanism, as proposed by Eliashberg [13] takes into account the retardation effects of the electron phonon interaction. This requires the evaluation of the electron self energy due to electron - phonon interaction and its effects

on the Cooper pairing in a self consistent manner. In going so the vertex corrections (Fig. 11.) are neglected by invoking Migdal's theorem. The validity of the theorem is usually justified in normal

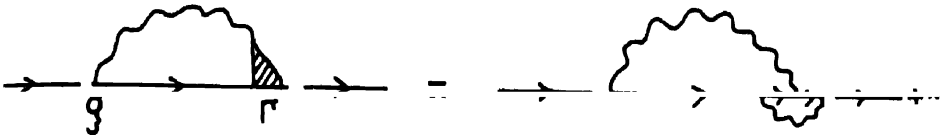


Fig.11. The modification of the electron self-energy by the vertex corrections due to electron-phonon interaction when the Migdal theorem breaks down. The full line represents the electron propagator, the wavy line the phonon propagator and the hatched region the full vertex correction, whose lowest order diagram is shown in the right hand side.

metals where the phonon frequencies being of the order of milli electron volts, the Debye temperature (θ_D) is a couple of 100K, while the fermi energy being of the order of an electron volt results in a Fermi temperature (T_F) of 10,000K. Thus the ratio of the energies involved i.e. $(\omega_D/\epsilon_F) = (\theta_D/T_F) \sim 10^{-2}$ which is rather a small parameter for normal metals, because of which the vertex corrections can be neglected in the calculation of the self energy of the electron due to electron-phonon interaction. On the other hand for the alkali doped fullerenes, the frequencies of the molecular vibrations are as high as 1500 cm^{-1} ($\sim 200 \text{ meV}$), while the fermi energy in the case of A_3C_{60} corresponds to half filling of the narrow t_{1u} band of width 0.5 eV i.e. $\epsilon_F \sim 0.25 \text{ eV} = 250 \text{ meV}$. Thus the Debye frequency and the Fermi energy are of the same order of magnitude, which makes the ratio $(\omega_D/\epsilon_F) \sim 1$. It is therefore obvious that Migdal's theorem is no longer valid for the alkali doped fullerenes. Hence a proper strong coupling theory must take into account the contribution from the vertex corrections to the self energy of the electron. Similarly there may be corrections arising from the renormalization of the phonon frequencies due to the electron phonon interaction.

Yet another factor of great importance in the BCS theory of superconductivity or its strong coupling version is the effect of the Coulomb repulsion between the electrons. How does the weak phonon mediated attractive interaction between the electrons dominate over the Coulomb repulsion? The answer to this question lies in the fact that in a normal metal the charge of an electron is heavily screened by the other electrons. Because of the Coulomb repulsion between the electrons the electron density around the vicinity of an electron will be depleted which amounts to screening

the charge of the electron by surrounding it with a positive charge density. This will greatly reduce the effective coulomb interaction, and can make the repulsion smaller than the attraction due to phonon mediation. The screening of a charge in a metal, however is more effective the more free electron like (wide band) the metal is, in which case the electrons can quickly respond to the electric field of the charge. In contrast the conduction band of the alkali doped fullerides is rather narrow (~ 0.5 eV), while the t_{1u} states forming the band is three fold degenerate; giving rise to a large density of states. Under these circumstances it is expected that the screening will be poor, hence the coulomb repulsion will be large and can dominate over the phonon mediated attraction. Thus the effective interaction between the electrons is expected to be predominantly repulsive, which will be unfavourable to Cooper pairing. However, those favouring the phonon mechanism tend to point to the fact that there is the speghati of the filled bands of large width (~ 4 eV) lying just below the conduction band, all of which will be effective in screening the Coulomb interaction.

Thus in the alkali doped fullerides the parameters entering the phonon mechanism of superconductivity are pushed to their limit. Therefore it is necessary to reexamine the strong coupling theory of superconductivity and test its validity for these systems.

5.6 Purely Electronic Mechanism

Soon after the discovery of superconductivity in the alkali doped fullerides ; it was realized that there are some similarities between these and the other high T_c superconductors such as cuprates [10]. In particular in both the systems, the undoped materials are insulators and superconductivity appears only on doping these with charge carriers. Thus it looks as if in both the systems superconductivity appears on the verge of a insulator-metal transition. However, the cuprates in the undoped form are antiferromagnets, while the fulleride has a non magnetic ground state. Even then in the later system the bands being very narrow it is expected that the coulomb correlation could be strong. The basic difference between the two is that while the cuprates are predominantly two dimensional systems, the fullerides are three dimensional in nature. Moreover, the undoped cuprate is a Mott-Hubbard insulator, while the pristine fulleride is more like a band insulator.

In addition to the similarities and dissimilarities of the pristine fulleride to the cuprates, the doped fullerides exhibit some properties which can be taken to be an indication towards the im-

portance of electron correlations in these systems. It has been found that the alkali doped system A_4C_{60} is an insulator [22], which is contrary to the expectations from the band theory. Since the t_{1u} level is three fold degenerate it can accommodate six electrons, hence doping the system with 4-alkali atoms will partially fill the t_{1u} band, which should then be a metal as per the dictates of band theory. There are several possible explanations for the insulating behaviour of A_4C_{60} . One of these is to invoke strong electron correlations, which could drive the system to a Mott - insulator. Or else it could be that the system undergoes the transition to a charge density wave (CDW) state with a suitable wave vector so as to open a gap at the Fermi surface. This can be anticipated from the evidence for (i) the existence of nested pieces of Fermi surface [23] and (ii) strong electron-phonon interaction discussed earlier. The other piece of information which again could point towards the presence of strong correlations in these systems is the observation that on doping the fullerenes with organic donors like $TDAE$ - molecules, the system $(TDAE) - C_{60}$ becomes a ferromagnet with a rather high Curie temperature of $16K$ [24]. This is perhaps the highest transition temperature for an organic ferromagnet. An explanation of the magnetism in the system may again require electron correlations to play an important role.

Therefore models of superconductivity based on purely electron correlation were proposed by Baskaran and Tosati [12] and also by Chakravarty, Gelfand and Kivelson [25]. The starting point in such theories is the single band Hubbard model [26], suitably defined for the truncated icosahedral C_{60} molecule, which is given by,

$$H = - \sum_{\langle ij \rangle \sigma} t (c_{i\sigma}^\dagger c_{j\sigma} + h.c) - \sum''_{\langle ij \rangle \sigma} t' (c_{i\sigma}^\dagger c_{j\sigma} + h.c) + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (3)$$

where t and t' are the hopping integrals for the long bonds in the pentagon and the short bonds joining the hexagons respectively while U is the intratomic coulomb repulsion and the other quantities carry their usual meaning. The values of the parameters in the model are estimated to be $t \sim 2$ to 3 eV, the onsite coulomb repulsion $U \sim 5$ to 10 eV and $1.0 < t'/t < 1.3$. It has been argued earlier by Anderson [27] that in the limit of large U , the ground state of the system described by the Hamiltonian of equation (3) is the resonating valence bond (RVB) state, which supports pair binding. Furthermore in the RVB ground state the elementary excitations correspond to those having a separation of spin and charge [28]. It was shown by Chakravarty et. al, that due to this composite nature of the electron consisting of an 'eion' of charge 'e' with no spin and a spinon of spin $1/2$ but no charge, it is energetically favourable for two of the injected electrons to stay on one

fullerene molecule while there is none on the other, rather than the configuration of each with one electron. Thus the electrons form real space pairs whose motion gives rise to the superconductivity in the alkali doped fullerenes. This argument can be visualized as follows : Let ϕ_0 and $\phi_n = \phi_0 + E_n$ be the energies of the ground states corresponding to the neutral molecule (C_{60}) and the energy of the molecule with n electrons respectively. Then the pair binding energy becomes

$$E_{pair} = 2E_1 - E_2 = 2\phi_1 - \phi_2 - \phi_0 \tag{4}$$

so that the pairing becomes attractive if $E_{pair} > 0$. In terms of the eon and the spinon the energy to add one electron to the molecule equals the sum of the creation energies E_e and E_s respectively of the two plus the eon-spinon interaction V_{es} , i.e

$$E_1 = \phi_1 - \phi_0 = E_e + E_s + V_{es} \tag{5}$$

Similarly the energy to add two electrons to a fullerene molecule in the singlet state becomes $2E_s$, because two spinons in the singlet state annihilate. It has also been assumed that the eon-eon and spinon-spinon interactions are negligible. Hence the pair binding energy can be written as

$$E_{pair} = 2E_1 - E_2 = 2(E_e + E_s + V_{es}) - 2E_e = 2(E_s + V_{es}) \tag{6}$$

and when $(E_s + V_{es}) > 0$ singlet pairing should be attractive. That is, it is energetically favourable to add two electrons to one C_{60} than to add one electron to each of the two fullerene molecules. Chakravarty et. al [25] have quantified this argument by using the Hubbard model, and obtain the pair binding energy in terms of U and t from second order perturbation theory as

$$E_{pair} = -0.05U + 0.015(U^2/t) + \dots \tag{7}$$

For reasonable values of U and t , $E_{pair} > 0$, i.e, pairing of electrons on a single fullerene molecule is favourable. The attractive pairing energy suggests that electron correlation on C_{60} can give rise to superconductivity. Assuming that the conduction band width W is large compared to the pair binding energy, the corresponding transition temperature is given by

$$T_c \propto \exp[-W/E_{pair}] \tag{8}$$

Thus the model predicts that the T_c should change if there are inter or intra molecular perturbations which would independently effect W or E_{pair} respectively. At the outset one of the seemingly

apparent drawbacks of the electronic mechanism of the superconductivity in the alkali doped fullerenes is the reconciliation of the model with the observed isotope shift. However, Chakravarty et. al, [29] have argued that even the isotope effect can be understood in terms of the electron mechanism, simply because the hopping integral t will change on isotopic substitution. On replacing ^{12}C by ^{13}C the zero point energy decreases due to the increase in the mass, this will shorten the bond lengths thereby increasing the overlap of the orbitals and hence t . On increasing t , E_{pair} decreases (as evident from equation (7)) and consequently T_c is suppressed, which follows from equation (8). Thus there will be an isotope shift. The estimated values of α shows reasonable agreement with the experimental value. Hence the electronic mechanism can not be ruled out based on the experimental observation of isotope effect.

In conclusion, it will be fair to state that even though there is a lot of experimental evidence which indicate in favour of the phonon mechanism of superconductivity, in the alkali doped fullerenes, the electronic mechanism can not be completely ruled out. In fact superconductivity in these systems may owe its origin to an interplay of electron-phonon interaction and electronic correlation.

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About the Reviewer

S. N. Behera did his M.Sc. in Physics in 1962 from Ravenshaw College Cuttack and Ph.D from the Indian Institute of Technology Kanpur in 1967. His field of specialization is theoretical Condensed Matter Physics. He has made original contributions in the areas of phonons in alloys and mixed crystals, structural phase transition in ferroelectric solids, Spin density wave (SDW) state in Chromium and its alloys, coexistence of superconductivity with charge and spin density wave states, Raman scattering in superconductors, Strongly correlated systems etc. and has published around sixty papers. He is currently interested in the phenomenon of high temperature superconductivity. He has edited two books entitled "Electronic Correlation and Disorder Effects in Metals" and "Clusters and Nanostructured Materials". Presently he is a professor at the Institute of Physics, at Bhubaneswar, the position he holds since 1989. He has visited several Universities and Institutions abroad, in different capacities.