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Conductivity and Superconductivity in C₆₀ Fullerides

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Abstract. — Conductivity and superconductivity of C₆₀ fullerides are reviewed, and the specific features of these new materials are described from the viewpoint of electronic properties and structure.

1. Introduction

Since the first observation of superconductivity in elemental metals such as Mercury by Onnes at the beginning of this century, many conventional and exotic conductors and superconductors have been discovered. From materials point of view, these superconductors can be broadly categorized as intermetallic, higher T_c oxide, inorganic polymer and organic superconductors [1]. The binary intermetallics include Nb₃M_{IV} (M_{IV} denotes Ge, Sn and Pb *etc.*) and V₃M_{III} (M_{III} denotes the Ga and Al *etc.*), where the highest transition temperature is observed in Nb₃Ge. Recently ternary and quaternary boron containing intermetallic compounds have been surveyed and T_c has been raised to 23 K [2]. In the seventies, (Ba, K)BiO₃ oxides were found and T_c was improved to 30 K. The critical transition temperature was raised dramatically with the discovery of two new families of copper oxides, La_{2-x}M_xCuO_{4-y} (M = Ca, Sr and Ba) with T_c 's of about 40 K and LnBa₂CuO_{7-x} (Ln = Y and/or other lanthanide's) with T_c 's of about 90 K [3]. A unique (SN)_x inorganic polymer superconductor was also found in 1975 [4]. Molecular conductors and superconductors have been actively studied since Little [5] proposed the exciton mechanism. Charge-transfer type molecular compounds have been searched, which has led to the finding of the first (TMTSF)PF₆ (TMTSF: tetramethyl-tetraselena-fulvalene) organic superconductor and afterward BEDT-TTF (BEDT-TTF: bis-ethylene-di-thiotetrathiafulvalene) superconductors [6].

One of the important issues in molecular conductors and superconductors is the dimensionality. Because of their low dimensionality, many organic conductors undergo metal-insulator transitions at low temperature before showing superconductivity. This is due to the instability of the ground states, causing the formation of charge-density-wave (CDW) or spin-density-wave

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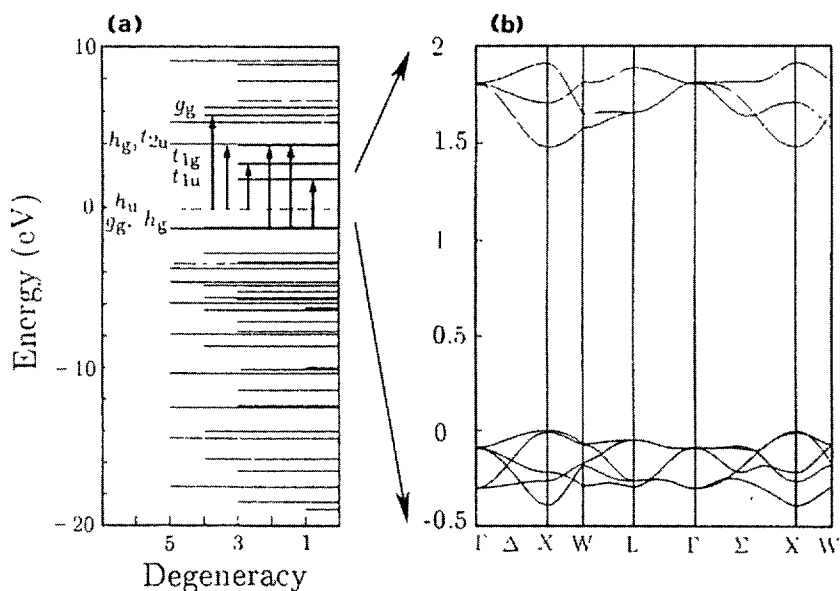


Fig. 1. — Band structure of fcc C₆₀ solid. Reproduced from reference [82]. Copyright 1992, American Physical Society.

(SDW). When C₆₀ was discovered [7,8], it was natural that a surge of interests arose since C₆₀ solid is three-dimensional and exhibits high symmetry [8]. Actually metallic properties were found when alkali metals were doped into C₆₀ solids [9] and subsequently superconductivity with relatively high T_c was reported [10]. Since then various electron donors have been doped into C₆₀ and T_c has reached at 30 to 40 K [11,12].

This review covers the structure and the electronic properties of pristine and doped fullerenes. Conductivity and superconductivity of A_xC₆₀ (A is alkali metal) fullerenes are discussed and compared to those encountered in the conventional superconductors.

2. Electronic States of C₆₀ Cluster and its Solid

The HOMO of the C₆₀ molecule has five degenerate levels with h_u symmetry and the LUMO with t_{1u} symmetry is triply degenerate. Since the five HOMO levels are completely occupied by ten electrons, C₆₀ has a closed-shell electronic structure. The orbitals forming these levels are p-type and the electrons delocalize over the molecule. In solid states C₆₀ cluster forms an fcc crystal. In solids the HOMO and the LUMO levels form bands as shown in Figure 1. The higher edge of the valence band consists of the h_u -derived levels and the lower edge of the conduction bands is made of the t_{1u} -derived levels. The reported band gap of the C₆₀ solid, categorized as a wide gap semiconductor, varies from 1.8 to 2.5 eV depending on the computational and experimental methods used.

Two general approaches can be undertaken for carrier injection. One is substituting some C₆₀ molecules with either electron-rich or electron-poor clusters. This is the same method used for silicon. For example, a P-type or N-type semiconductor forms when Si is replaced with either B or P. In the case of fullerenes, BC₅₉ and NC₅₉ clusters can be considered for hole and electron injection, and endohedral molecules such as La³⁺C₈₂³⁻ [13–15] can also be used.

However, no such experiments have been reported so far. The other method is intercalation, as often used in the two dimensional analog system, graphite. A wide variety of species can be intercalated into the van der Waals galleries between the adjacent graphene sheets. Some of the graphite intercalation compounds, such as KC₈, are known to be superconducting with very low T_c [16]. In contrast to the two dimensional graphite, C₆₀ solid is three-dimensional, with large interstitial site spacings that can accommodate intercalants. C₆₀ intercalation compounds with alkali-metals [9,10], alkaline earth metals [17,18] and some of other rare-earth elements [19,20] have been reported.

3. Conductivity and Superconductivity in Doped Fullerenes

Haddon and coworkers [9] first reported high conductivity in alkali metal doped C₆₀ and C₇₀, where they found that the conductivity first increases and then decreases with increasing doping time. Follow-up experiments show that the maximum conductivity occurs at $x = 3$ [21]. Temperature dependent measurement shows that K₃C₆₀ and Rb₃C₆₀ solids are metallic [22]. Subsequent experiments by Hebbard and coworkers [10] show superconductivity in K₃C₆₀ with an onset temperature of 18 K. The relatively high T_c in K₃C₆₀ has created considerable excitement in the scientific community. Since then the T_c for C₆₀ fullerenes has been raised up to 33 K [11,12,23] at 1 bar and 40 K under pressure [24]. Alkaline-earth metals have also been intercalated into the C₆₀ lattice [17,18,25]. Superconductivity has been observed in Ca₅C₆₀ (8.4 K), Ba₆C₆₀ (6 K) and Sr₆C₆₀ (4 K). Transport measurements show that conductivity of C₆₀ film increases with Ba doping level and reaches a maximum at roughly five to six Ba atoms per C₆₀ [26]. Rare-earth element Yb doping was achieved by Ozdas *et al.* [19] and T_c of 6 K was observed at $x = 2.75$. The electronic behavior of Eu-C₆₀ system has been studied by XPS and UPS, and metallic possibility is presented [20]. Recently, structure and superconductivity of Sm doped C₆₀ is reported. La doped C₆₀ is reported to superconduct at 12 K, but the structure and the stoichiometry have not been determined and the superconducting fraction is quite small.

The possibility of hole doping has been explored, but without any success. Higher fullerenes such as C₇₀, C₇₆ and C₈₂, have also been used as the host for intercalation. Although some compounds show signs of metallic behavior, no superconductivity has been observed so far.

4. Structure and Stability of C₆₀ Fullerides

C₆₀ forms a van der Waals crystal in the solid state, reflecting the fact that it is a closed shell molecule with a relatively large gap between HOMO and LUMO. It is important to note that the covalent character of the C₆₀ solid is relatively stronger than that of the conventional van der Waals organic crystals when considering the optical and electronic properties of C₆₀ solids.

Since the icosahedral point group $I_h(m\bar{3}5)$ of the fullerene molecule is incompatible with the periodic translational symmetry, there are only two ways to incorporate it into a crystal lattice: 1) the molecule itself undergoes a symmetry breaking to a lower symmetry configuration that is consistent with the crystal symmetry; 2) the molecule is disordered. Single crystal X-ray diffraction measurements by Fleming and co-workers [27] show that at room temperature the C₆₀ molecules crystallize into a face-centered cubic structure with the fullerene molecules residing at the corner and the face-center positions of the cubic unit cell. The apparent symmetry deduced from the X-ray data is $Fm\bar{3}m$, in which the fullerene molecules are orientationally disordered [28]. The simplest way to pack C₆₀ into an fcc unit cell is to let all the molecules have the same orientation, with the unit cell translational vectors passing through three orthogonal 2-fold axes (hexagon-hexagon edge). This orientationally ordered packing gives a

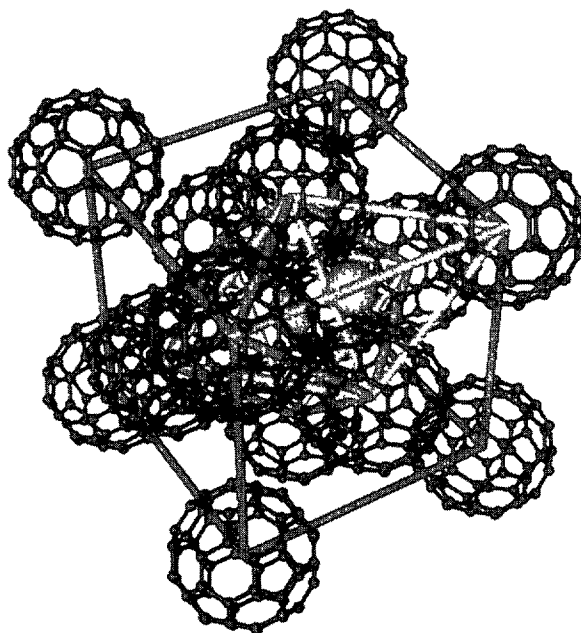


Fig. 2. — Structure of fcc C_{60} solid. In this figure, O- and T-sites are shown.

lattice with $Fm\bar{3}$ symmetry. There are two ways to orient the molecules into such a configuration, which are related by a 90 degree rotation. It is argued that the observed $Fm\bar{3}m$ symmetry arises from the random occupancy of these two symmetry-equivalent orientations. Nuclear magnetic resonance (NMR) measurement by Tycko *et al.* indicates that the fullerene molecules are in dynamically disordered with almost unhindered rotation at room temperature and in jumping reorientation at low temperature. Synchrotron X-ray diffraction study by Heiney and co-workers show that there is a phase transition around 255 K, from orientationally disordered fcc at high temperature to an orientationally ordered simple cubic structure at low temperature [29–42].

In the fcc unit cell, there are two types of interstitial vacancies: the smaller tetrahedral (T-) (two per C_{60}) and the larger octahedral (O-) (one per C_{60}) sites, as shown in Figure 2. When alkali metals are intercalated into the fcc lattice, they occupy these interstitial sites. If one ignores the molecular orientation, four distinct crystalline structures can form without alternating the host structure: (i) the rock salt type (A_1C_{60}) in which all O-sites are singly occupied; (ii) the anti-fluorite type (A_2C_{60}) in which all T-sites are occupied; (iii) A_3C_{60} where all the T- and O-sites are occupied; and (iv) A_1C_{60} with half of the T-sites are selectively occupied (this has only been observed in the metastable Na_1C_{60}). Most of the superconducting alkali metal fullerenes have the same chemical composition of A_3C_{60} ($A = K$ and Rb) and the face-centered cubic (fcc) structure, at least at room temperature. Two exceptions are the Cs_3C_{60} [24] and the $NH_3K_3C_{60}$ [43]. Both have non-fcc structure and are only superconducting under hydrostatic pressure. In these compounds the charge transfer from alkali metal to C_{60} is almost complete, resulting a nearly triply minus-charged C_{60}^{3-} molecule. This is due to the low ionization energy of A and the relatively large electron affinity of C_{60} [44,45]. The crystal structure of the superconducting K_3C_{60} was determined by Stephens *et al.* [46]. In the fcc K_3C_{60} cell, the fullerenes are randomly distributed between the two symmetry equivalent orientations, as described earlier, resulting in an apparent $Fm\bar{3}m$ symmetry [46].

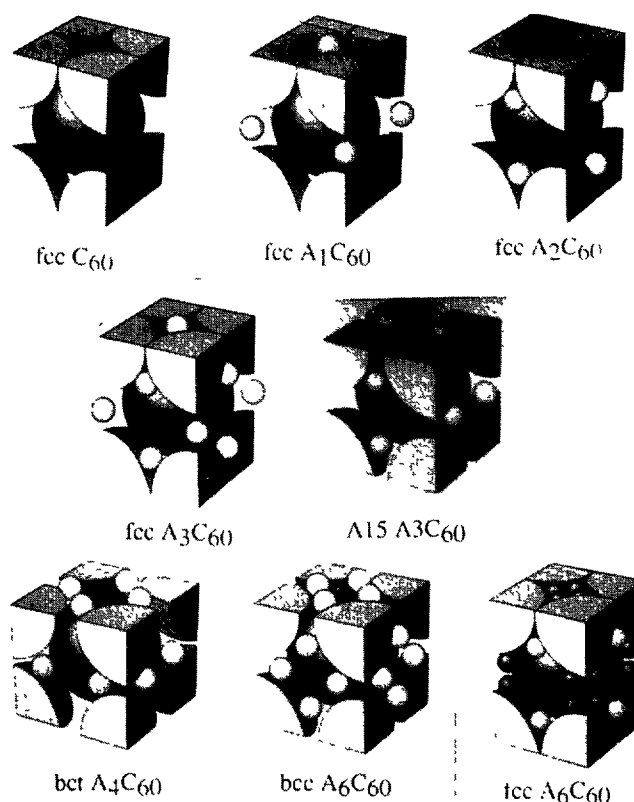


Fig. 3. — Various crystal phases found in C_{60} fullerenes. In $fcc\ A_6C_{60}$ the Na_4 cluster is accommodated in the larger octahedral site. A15 phase is found when alkaline-earth elements are intercalated. Cs_3C_{60} is classified into either A15 or cation-vacant type bct. Reproduced from reference [11] with modifications. Copyright 1992, Pergamon Press.

Increasing the alkali metal concentration beyond 3 per C_{60} distorts the C_{60} host structure, first to body-centered tetragonal (bct) at $x = 4$ ($A = K, Rb$ and Cs) [47], then to body centered cubic (bcc) at $x = 6$ ($A = K, Rb$ and Cs) [48] as seen in Figure 3. For smaller alkali metal Na , the fcc structure of the host lattice persists up to 11 Na/C_{60} . In Na_6C_{60} [49] and $Na_{11}C_{60}$ [50], Na_4 and Na_9 clusters form in the large fcc octahedral sites, respectively. For the largest alkali metal Cs and divalent metal Ba , in addition to the stable bcc Cs_6C_{60} [48] and Ba_6C_{60} [18] phases, an A15 phase forms at $x = 3$ [24, 51]. Although lithium intercalation has not been studied in detail, preliminary data show that, unlike the other A_3C_{60} compounds, Li_3C_{60} adapts a hexagonal closed packed structure [52].

In the isostructural A_3C_{60} series, a wide variation in lattice parameters can be achieved by choosing the appropriate intercalants. In general the lattice parameter is proportional to the total cation volume, as depicted in Figure 4. Several anomalous behaviors are also observed. First, $fcc\ A_3C_{60}$ structure does not form for the largest and the smallest cations, Cs and Li . Although metastable Cs_3C_{60} with A15 and bct structure has been synthesized at low temperature [24], it disproportionates to the thermodynamically more stable Cs_1C_{60} and Cs_4C_{60} if it is annealed above 473 K. In a similar fashion, KCs_2C_{60} is not stable. Second, a significant deviation from the monotonic relation is observed when small alkali Na resides in the octahedral site, as in the case of Na_3C_{60} [49]. This deviation starts from Na_2KC_{60} [53].

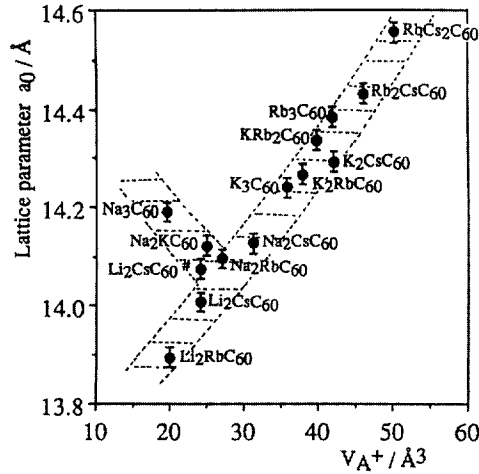


Fig. 4. — The relationship between the cubic lattice constant a_0 and the total volume (V_A^+) of the intercalated alkali cations in A_3C_{60} . The fcc cell is taken as an equivalent bct cell with $a_{bct} = a_{fcc}$.

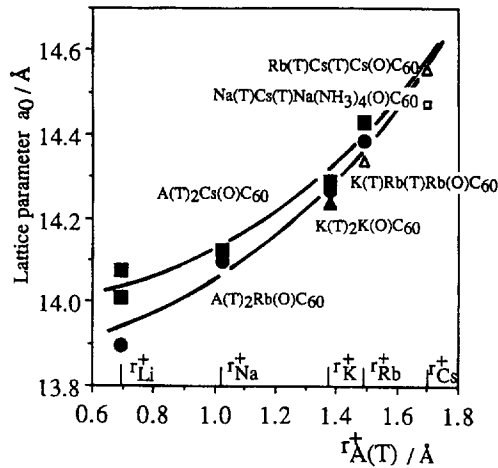


Fig. 5. — The lattice parameters of a_0 as a function of the alkali-metal ionic radius in T-site. The lattice size is well parametrized by the alkali-metal ionic radius in T-site with little influence of it in O-site.

As discussed earlier, there are two types of interstitial vacancies in the fcc structure: 2 small T-sites and 1 large O-site per C_{60} . When mixed alkali metals are intercalated, in general the larger cations occupy the O-sites and the smaller ones the T-sites. An example is Na_2CsC_{60} in which the two larger cations are accommodated in the O-sites and the smaller ones in the T-sites. This site selectivity has been shown by both X-ray [54] and NMR measurements [55]. In general one finds that the structure is more stable with such a distribution of un-even sized cations. From simple geometric argument, we also expect that the lattice parameters are controlled by the ionic radii of alkali cations in the T-sites [53] as illustrated in Figure 5, where the lattice parameters are plotted as a function of the ionic radius of the alkali metals in the tetrahedral sites. The ternary $Na(NH_3)_4(O)Na(T)Cs(T)C_{60}$ [54] also lies on the line depicted in this figure, supporting the above correlation.

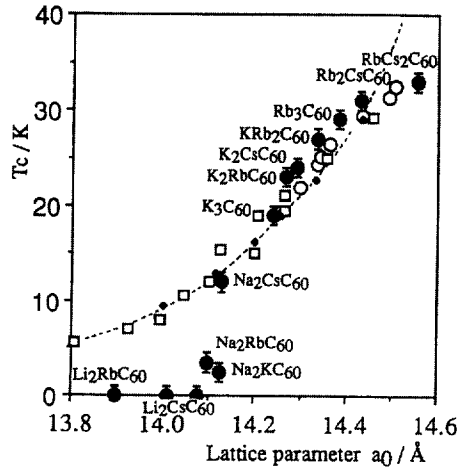


Fig. 6. — The relationship between the superconducting transition temperature T_c and the cubic lattice constants a_0 of A_3C_{60} ($A = \text{Li, Na, K, Rb, Cs}$ and their mixtures) salts over a wide range of a_0 . Data indicated by open and closed circles are experimental data. The solid line is the fitted curve to the both sets of data. The open triangles and squares are the relationships for K_3C_{60} and Rb_3C_{60} obtained from high pressure experiments and the dotted line is the $T_c - a_0$ relationship expected from the simple BCS theory using N_{E_F} values by LDA calculations. The relationship is classified by the three types of superconducting crystal phases: fcc A_3C_{60} in the large lattice size region, sc A_3C_{60} in the small lattice size region showing large drop in T_c and non-superconducting Li_2AC_{60} fullerenes.

5. Conventional and Unconventional Pictures in Electronic Properties of C_{60} Fullerides

The simple scenario of superconductivity in the BCS framework and the easy control of lattice parameters described earlier have provided researchers with a very successful guideline in the attempts to raise the T_c of A_3C_{60} metallic fullerenes [11, 12] by lattice expansion through the increase of the ionic radii of the alkali-metal cations. The higher T_c in C_{60} based superconductors has simply been sought for alkali-metal C_{60} fulleride by changing the alkali-metal dopants that can be accommodated in the interstitial sites in order to change the lattice parameters. The simple 3-D structure of a series of superconductors with the change in lattice parameter is also anticipated to give important information for understanding the origin of this high T_c superconductivity.

In Table I we list all the known superconducting C_{60} fullerenes, and their respective transition temperature is plotted *versus* the lattice parameter (a_0) in Figure 6. The T_c 's of these compounds vary from 3.5 K (Na_2RbC_{60}) [56, 57] to 33 K ($RbCs_2C_{60}$) [23]. The highest T_c of 33 K at 1 bar is only surpassed by the high- T_c copper oxide superconductors [11, 12]. The plot shows a clear monotonic relation between the transition temperature and the unit cell parameter (which reflects the inter-molecular spacing), suggesting a BCS type superconducting mechanism where T_c is mainly controlled by the density of states at the Fermi level [58, 59]. In the framework of the Bardeen-Cooper-Schrieffer (BCS) theory, T_c is expressed as

$$T_c = 1.13h/2\pi\langle w \rangle / k_B \exp[-1/(N_{E_F} V)].$$

Here, $\langle w \rangle$ is the cut-off frequency of related phonons and V denotes the coupling constant between phonons and electrons. The density of state increases through band narrowing when

Table I. — *Lattice constants and position of the alkali elements for A_3C_{60} fullerenes at ambient temperature.*

A_3C_{60}	$a_0(\text{\AA})$	$A_1(T)A_2(T)A_3(O)$	Type	$T_c(K)$
Cs_3C_{60}	—		A15, bct	40 ^a
$RbCs_2C_{60}$	14.555	$Rb(T)Cs(T)Cs(O)$	fcc	33
KCs_2C_{60}	unstable		fcc	—
Rb_2CsC_{60}	14.431	$Rb(T)Rb(T)Cs(O)$	fcc	31
Rb_3C_{60}	14.384	$Rb(T)Rb(T)Rb(O)$	fcc	29
KRb_2C_{60}	14.337	$K(T)Rb(T)Rb(O)$	fcc	27
K_2CsC_{60}	14.292	$K(T)K(T)Cs(O)$	fcc	24
K_2RbC_{60}	14.267	$K(T)K(T)Rb(O)$	fcc	23
K_3C_{60}	14.240	$K(T)K(T)K(O)$	fcc	19
Na_2CsC_{60}	14.126	$Na(T)Na(T)Cs(O)$	fcc	12
Na_2RbC_{60}	14.092	$Na(T)Na(T)Rb(O)$	fcc \rightarrow sc	3.5
Na_2KC_{60}	14.122	$Na(T)Na(T)K(O)$	fcc \rightarrow sc	2.5
Na_3C_{60}	14.191	$Na(T)Na(T)Na(O)$	fcc ^b	< 2K
Li_2CsC_{60}	14.075	$Li(T)Li(T)Cs(O)$	fcc	< 50 mK
$Li_2CsC_{60}^\#$	14.008	$Li(T)Li(T)Cs(O)$	fcc	< 50 mK
Li_2RbC_{60}	13.896	$Na(T)Na(T)Rb(O)$	—	< 50 mK
Li_2KC_{60}	multiphase	—	—	—
$Na_2Cs(NH_3)_4C_{60}$	14.473	$Na(T)Cs(T)Na(NH_3)_4(O)$	fcc	30
Ba_6C_{60}	11.182		bcc	6
Sr_6C_{60}	10.975		bcc	4
Ca_5C_{60}	14.01		sc	8.5
$Yb_{2.75}C_{60}$	superlattice		orthorhombic	6
$Sm_{2.75}C_{60}$	superlattice		orthorhombic	8

^a Under hydrostatic pressure.^b Stable at $T > 180$ K.

A different batch of samples.

the inter-molecular separation is raised through lattice expansion. The same conclusion can also be seen in the pressure dependent T_c measurements [60–62]. Such a phonon-mediated BCS mechanism is also indicated by the observed isotope experiments [63–66] — the substitution of ^{12}C by ^{13}C in C_{60} reduces T_c as shown in Figure 7. Furthermore, the fact that no isotope effects of $^{87}Rb/^{85}Rb$ in T_c is observed as seen in Figure 7 also supports the same idea.

For further clarification, the density of states at the Fermi level (N_{E_F}) and phonons modes in the fullerene superconductors have been investigated in detail by a variety of techniques, both experimentally and theoretically. N_{E_F} can be estimated from the Korringa relationship in ^{13}C -NMR [67, 68], magnetic susceptibility in SQUID after correcting the spin-orbital Landau diamagnetic susceptibility as well as the diamagnetic contribution from the alkali-metal

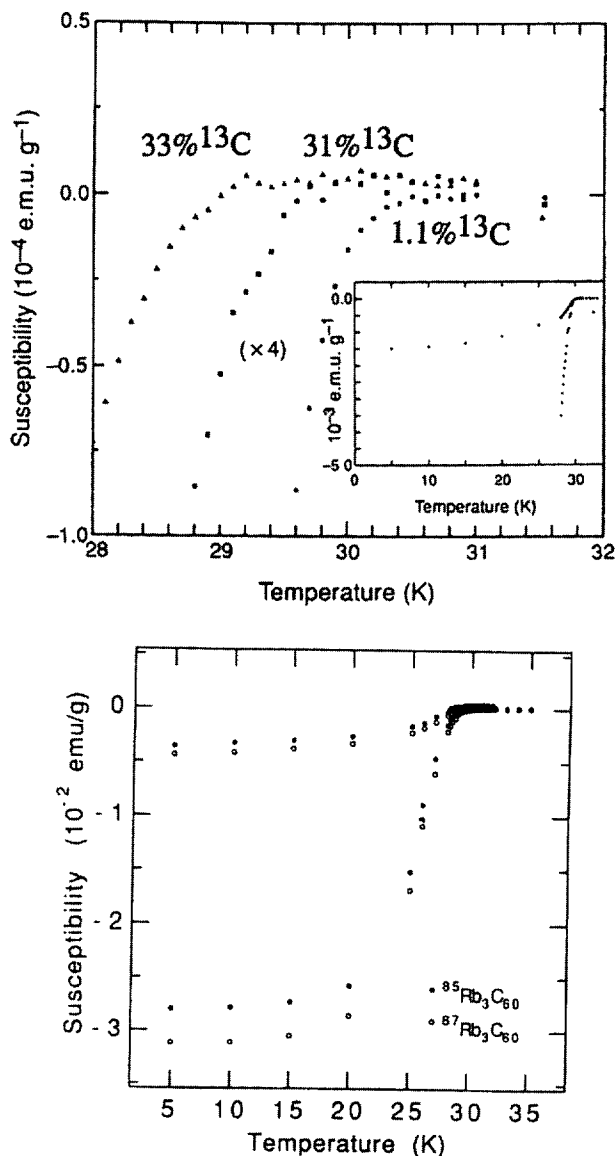


Fig. 7. — Isotope effects of ^{13}C and ^{87}Rb on superconducting transition temperature in Rb_3C_{60} .

cations [69], spin susceptibility in ESR [70–72], optical reflectivity [73,74] and thermoelectric power [75]. ^{13}C -NMR studies show that N_{E_F} increases as the lattice expands, supporting the scenario that N_{E_F} is the most important parameter for T_c in A_3C_{60} . The same conclusion has been obtained from ESR, thermoelectric power measurements and optical reflection spectroscopy. It should be noted that UPS measurements [76] report smaller N_{E_F} values than those obtained by the other techniques.

Information regarding the phonons can be obtained by either raman [77,78] or neutron [79,80] spectroscopy. Significant changes in the phonon frequencies and intensities are observed

Table II. — *Physical properties of K_3C_{60} and Rb_3C_{60} superconductors.*

	K_3C_{60}	Rb_3C_{60}
a_0 (Å)	14.240	14.384
ρ ($\Omega \text{ cm}^{-1}$)	2×10^{-3}	1×10^{-2}
T_c (K)	19	29
dT/dP ($K^{-1} \text{ GPa}^{-1}$)	-0.97 -0.78	
da_0/dP (GPa^{-1})	1.20×10^{-2}	1.52×10^{-2}
H_{c1} (mT)	13	26
H_{c2} (mT)	26	78
ξ (nm)	2.6	2.0
λ (nm)	240,480 600	168 440 460
l (Å)	31	9
$2\Delta/T_c$	4.0 3.6 3.6 5.2	3.1 3.0 3.0 5.3
N_{EF} ($\text{eV}^{-1} C_{60}^{-1}$)	15 ± 10	20 ± 10

principally for the intramolecular Hg vibrational modes, both in the high-energy tangential (130-200 meV) and the low-energy radial (roughly 50 meV) regions. Furthermore, the coupling strength (V) between phonons and electrons has been deduced from the phonon linewidth changes, and is reported to be 45.6 meV for K_3C_{60} . These observations, when combined with the observed T_c , the renormalized Coulomb interaction parameter ($\mu^* = 0.15$) and the density of states (14 states eV^{-1} mole C_{60}^{-1}), lead to the conclusion that the large average mean-phonon-frequency is as high as 1000 K.

Band structure calculations have been carried out for C_{60} and its related fullerenes [81–83]. In the solid states, the h_u HOMO and t_{1u} LUMO levels of C_{60} molecules overlap to form bands whose wavefunctions strongly retain the C_{60} molecular features [84,85]. Some important results regarding A_3C_{60} are summarized here. First, charge transfer from the alkali metal s orbital to the C_{60} t_{1u} -derived bands is almost complete. Consequently, no considerable distribution of conduction electrons is observed around the alkali metals. Thus the lower part of the conduction bands is roughly half-filled, resulting in a metallic ground state for A_3C_{60} with relatively high density of states at the Fermi level. Second, the band originated from the s-orbitals of the alkali-metals is located far above (about 2 eV) the Fermi level of the t_{1u} -conduction bands. Hence the electronic properties of A_3C_{60} can be best described as being primarily governed by the solid C_{60} states, while alkali metals function merely as electron donors.

The metallic properties observed in A_3C_{60} can be understood, using the band calculation result described above. When three electrons are injected into the conduction band, it becomes half filled with the Fermi level nearly at the top of the band to give a high density of states, rendering this composition metallic with higher conductivity than the other stoichiometries. The simple scenario described above seems to be able to roughly explain the superconductivity observed in alkali-metal C_{60} fullerenes. Important physical parameters experimentally obtained for K_3C_{60} and Rb_3C_{60} are summarized in Table II. These parameters seem to be consistent with the scenario described here.

Along the scenario, however, metallic properties are expected for A_xC_{60} with any stoichiometry of $0 < x < 6$ since the t_{1u} -derived conduction bands remain partially filled until six

electrons are introduced per C_{60} , Considering the fact that real metallic properties can only be found in the fullerenes with the stoichiometry A_3C_{60} and so does superconductivity, the real picture of the band structure of alkali-metal C_{60} fullerenes will be more complex.

When we look at the $T_c - a_0$ relationship more carefully, three features different from the above simple description are apparently clear. One is the unexpected steep decrease in T_c observed for A_3C_{60} in the small lattice parameter region. The T_c 's of 2.5-3.5 K observed for Na_2KC_{60} and Na_2RbC_{60} are considerably low far from the expectation simply extrapolated using the data of pressure experiments on K_3C_{60} and Rb_3C_{60} in the BCS framework. Their T_c 's should be around 8-10 K. The other is the saturation in T_c for A_3C_{60} with large lattice parameters. The slightly higher T_c could be expected than the T_c values of Rb_2CsC_{60} ($T_c = 31$ K) and $RbCs_2C_{60}$ ($T_c = 33$ K) considering their lattice parameters. Finally, both Li_2CsC_{60} and Li_2RbC_{60} are not superconducting, despite the apparent band filling by electron transfer into C_{60} solids. These phenomena cannot be explained by the simple description itself.

Other than alkali-metals as a source of electron carriers to give metallic and superconducting properties, alkaline-earth metals and rare-earth metals have so far given metallic fullerenes. It should be pointed out again that hybridization between C_{60} molecular t_{1g} levels and alkaline-earth s-levels plays an important role in leading these fullerenes to be metallic and superconducting. Although the details in crystal structure has become clear recently, the mechanism of superconductivity is still not well understood.

6. Concluding Remarks

New finding of high conductivity and superconductivity with high T_c only surpassed by copper oxide superconductivity for C_{60} based materials has resulted in a surge of interests in fundamental aspects in physics and chemistry as well as in a search for technological applications. Because of the simplicity of the C_{60} geometry and a variety of electronic properties found in different crystal structures, lots of studies have been attempted regardless of the difficulties in handling of these intercalation compounds in air. Details of the new solids made from C_{60} , which will be very difficult to obtain in other metallic and superconducting systems, have been clarified in a very short research period. It is needless to say that the reason of such speedy and vast numbers of studies is a result of scientifically accumulated previous knowledge in the past two decades, as well as recently expanded international collaborations. Exotic superconducting materials are hoped to be designed and synthesized in the near future from these basic studies.

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