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# Conductivity and Superconductivity in C<sub>60</sub> Fullerenes

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**Abstract.** — Conductivity and superconductivity of C<sub>60</sub> fullerenes 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 Nb<sub>3</sub>M<sub>IV</sub> (M<sub>IV</sub> denotes Ge, Sn and Pb *etc.*) and V<sub>3</sub>M<sub>III</sub> (M<sub>III</sub> denotes the Ga and Al *etc.*), where the highest transition temperature is observed in Nb<sub>3</sub>Ge. 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)BiO<sub>3</sub> 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<sub>2-x</sub>M<sub>x</sub>CuO<sub>4-y</sub> (M = Ca, Sr and Ba) with  $T_c$ 's of about 40 K and LnBa<sub>2</sub>CuO<sub>7-x</sub> (Ln = Y and/or other lanthanide's) with  $T_c$ 's of about 90 K [3]. A unique (SN)<sub>x</sub> 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)PF<sub>6</sub> (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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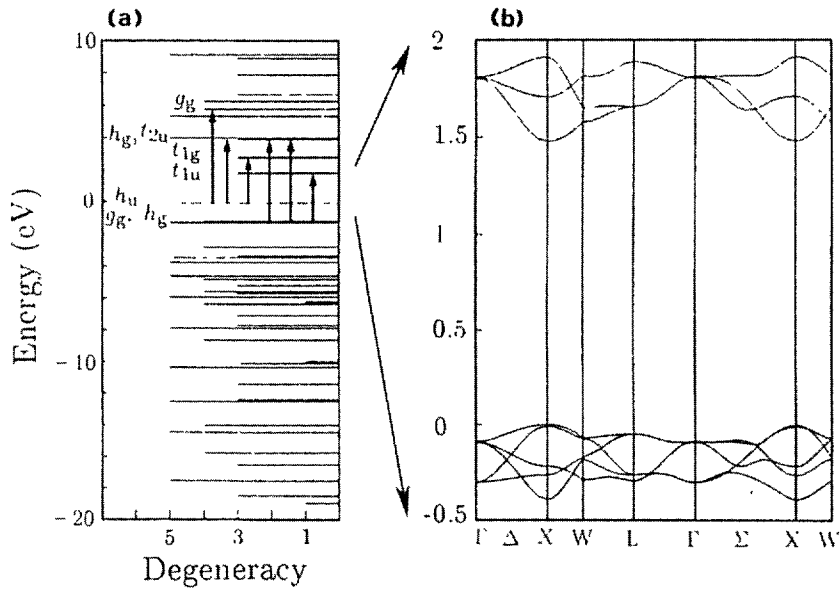


Fig. 1. — Band structure of fcc C<sub>60</sub> solid. Reproduced from reference [82]. Copyright 1992, American Physical Society.

(SDW). When C<sub>60</sub> was discovered [7,8], it was natural that a surge of interests arose since C<sub>60</sub> solid is three-dimensional and exhibits high symmetry [8]. Actually metallic properties were found when alkali metals were doped into C<sub>60</sub> solids [9] and subsequently superconductivity with relatively high  $T_c$  was reported [10]. Since then various electron donors have been doped into C<sub>60</sub> 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<sub>x</sub>C<sub>60</sub> (A is alkali metal) fullerenes are discussed and compared to those encountered in the conventional superconductors.

## 2. Electronic States of C<sub>60</sub> Cluster and its Solid

The HOMO of the C<sub>60</sub> 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, C<sub>60</sub> has a closed-shell electronic structure. The orbitals forming these levels are p-type and the electrons delocalize over the molecule. In solid states C<sub>60</sub> 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 C<sub>60</sub> 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 C<sub>60</sub> 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, BC<sub>59</sub> and NC<sub>59</sub> clusters can be considered for hole and electron injection, and endohedral molecules such as La<sup>3+</sup>C<sub>82</sub><sup>3-</sup> [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 KC<sub>8</sub>, are known to be superconducting with very low  $T_c$  [16]. In contrast to the two dimensional graphite, C<sub>60</sub> solid is three-dimensional, with large interstitial site spacings that can accommodate intercalants. C<sub>60</sub> 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 C<sub>60</sub> and C<sub>70</sub>, 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 K<sub>3</sub>C<sub>60</sub> and Rb<sub>3</sub>C<sub>60</sub> solids are metallic [22]. Subsequent experiments by Hebbard and coworkers [10] show superconductivity in K<sub>3</sub>C<sub>60</sub> with an onset temperature of 18 K. The relatively high  $T_c$  in K<sub>3</sub>C<sub>60</sub> has created considerable excitement in the scientific community. Since then the  $T_c$  for C<sub>60</sub> fullerides 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 C<sub>60</sub> lattice [17,18,25]. Superconductivity has been observed in Ca<sub>5</sub>C<sub>60</sub> (8.4 K), Ba<sub>6</sub>C<sub>60</sub> (6 K) and Sr<sub>6</sub>C<sub>60</sub> (4 K). Transport measurements shows that conductivity of C<sub>60</sub> film increases with Ba doping level and reaches a maximum at roughly five to six Ba atoms per C<sub>60</sub> [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-C<sub>60</sub> system has been studied by XPS and UPS, and metallic possibility is presented [20]. Recently, structure and superconductivity of Sm doped C<sub>60</sub> is reported. La doped C<sub>60</sub> 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 C<sub>70</sub>, C<sub>76</sub> and C<sub>82</sub>, 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 C<sub>60</sub> Fullerides

C<sub>60</sub> 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 C<sub>60</sub> solid is relatively stronger than that of the conventional van der Waals organic crystals when considering the optical and electronic properties of C<sub>60</sub> solids.

Since the icosahedral point group I<sub>h</sub>(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 C<sub>60</sub> 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 C<sub>60</sub> 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

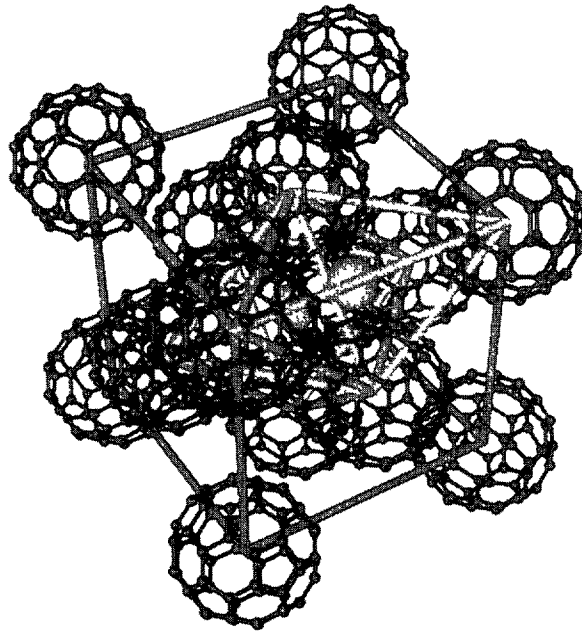


Fig. 2. — Structure of fcc  $C_{60}$  solid. In this figure, O- and T-sites are shown.

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].

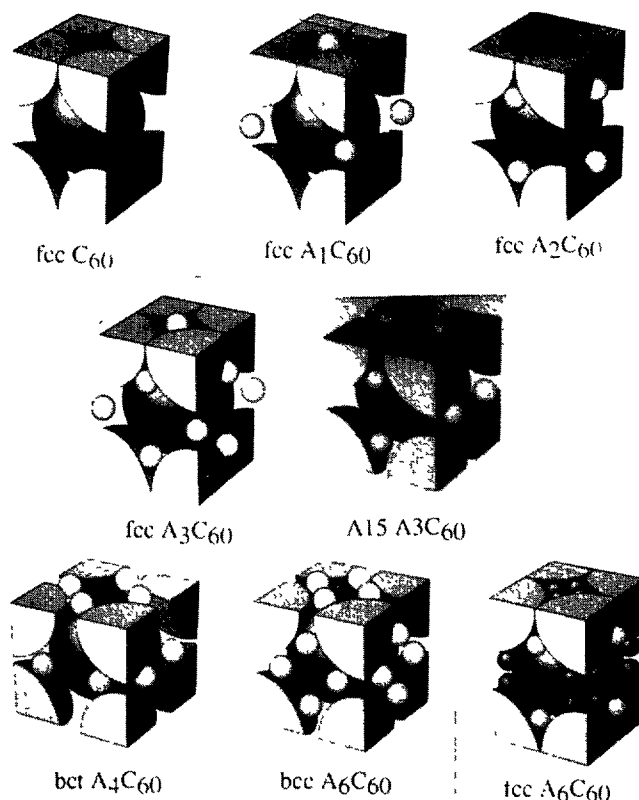


Fig. 3. — Various crystal phases found in  $C_{60}$  fullerenes. In  $fcc A_6C_{60}$  the  $Na_4$  cluster is accommodated in the larger octahedral site. A15 phase is found when alkaline-earth elements are intercalated.  $Cs_3C_{60}$  is classified into either A15 or cation-vacant type bct. Reproduced 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].

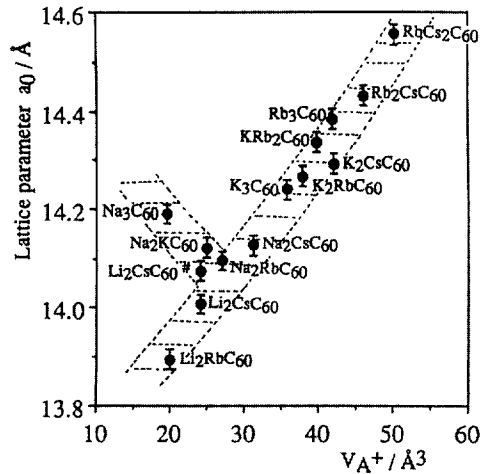


Fig. 4. — The relationship between the cubic lattice constant  $a_0$  and the total volume ( $V_A^+$ ) of the intercalated alkali cations in  $A_3C_{60}$ . The fcc cell is taken as an equivalent bct cell with  $a_{bct} = a_{fcc}$ .

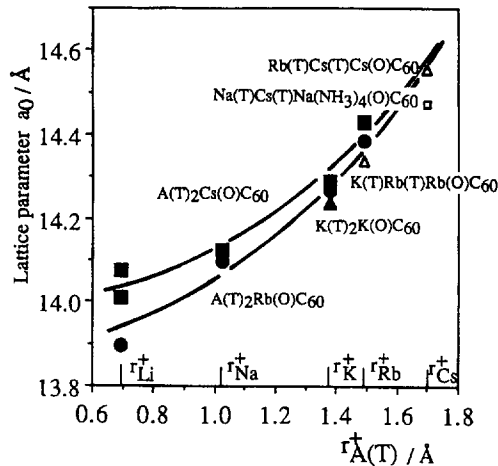


Fig. 5. — The lattice parameters of  $a_0$  as a function of the alkali-metal ionic radius in T-site. The lattice size is well parametrized by the alkali-metal ionic radius in T-site with little influence of it in O-site.

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.

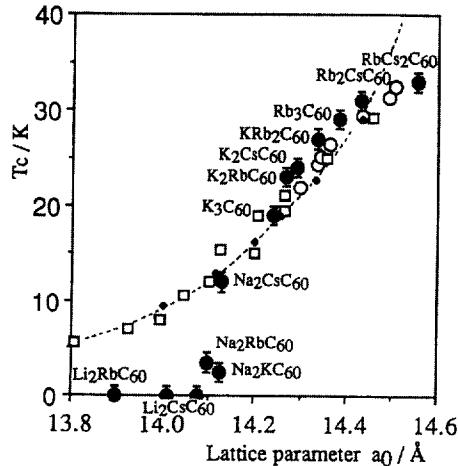


Fig. 6. — The relationship between the superconducting transition temperature  $T_c$  and the cubic lattice constants  $a_0$  of  $A_3C_{60}$  ( $A = \text{Li, Na, K, Rb, Cs}$  and their mixtures) salts over a wide range of  $a_0$ . Data indicated by open and closed circles are experimental data. The 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 fullerides [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  $C_{60}$  fullerides, 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.*

$A_3C_{60}$	$a_0(\text{Å})$	$A_1(T)A_2(T)A_3(O)$	Type	$T_c(K)$
$Cs_3C_{60}$	—		A15, bct	40 <sup>a</sup>
$RbCs_2C_{60}$	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 → sc	3.5
$Na_2KC_{60}$	14.122	Na(T)Na(T)K(O)	fcc → sc	2.5
$Na_3C_{60}$	14.191	Na(T)Na(T)Na(O)	fcc <sup>b</sup>	< 2K
$Li_2CsC_{60}$	14.075	Li(T)Li(T)Cs(O)	fcc	< 50 mK
$Li_2CsC_{60}$ <sup>#</sup>	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 <sub>3</sub> ) <sub>4</sub> (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

<sup>a</sup> Under hydrostatic pressure.

<sup>b</sup> Stable at  $T > 180$  K.

<sup>#</sup> 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

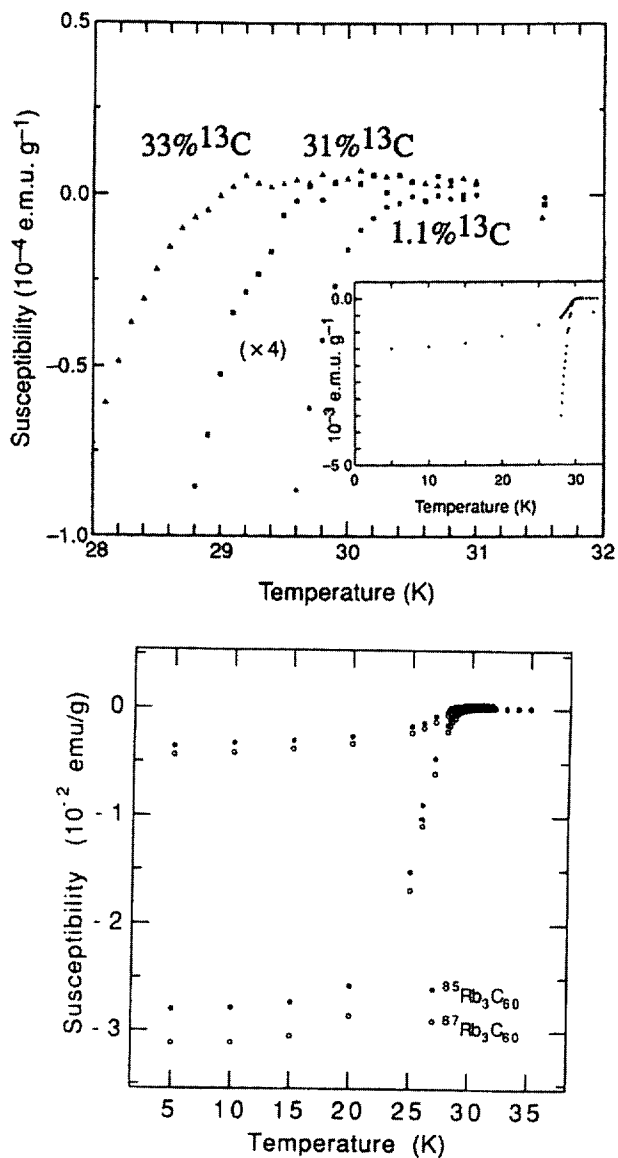


Fig. 7. — Isotope effects of  $^{13}C$  and  $^{87}Rb$  on superconducting transition temperature in  $Rb_3C_{60}$ .

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
$\rho$ ( $\Omega \text{ cm}^{-1}$ )	$2 \times 10^{-3}$	$1 \times 10^{-2}$
$T_c$ (K)	19	29
$dT/dP$ ( $\text{K}^{-1} \text{ GPa}^{-1}$ )	-0.97 -0.78	
$da_0/dP$ ( $\text{GPa}^{-1}$ )	$1.20 \times 10^{-2}$	$1.52 \times 10^{-2}$
$H_{c1}$ (mT)	13	26
$H_{c2}$ (mT)	26	78
$\xi$ (nm)	2.6	2.0
$\lambda$ (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
$N_{\text{EF}}$ ( $\text{eV}^{-1} \text{ C}_{60}^{-1}$ )	$15 \pm 10$	$20 \pm 10$

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  $\text{eV}^{-1}$  mole  $\text{C}_{60}^{-1}$ ), 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<sub>60</sub>, Considering the fact that real metallic properties can only be found in the fullerenes with the stoichiometry A<sub>3</sub>C<sub>60</sub> and so does superconductivity, the real picture of the band structure of alkali-metal C<sub>60</sub> 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<sub>3</sub>C<sub>60</sub> in the small lattice parameter region. The  $T_c$ 's of 2.5-3.5 K observed for Na<sub>2</sub>KC<sub>60</sub> and Na<sub>2</sub>RbC<sub>60</sub> are considerably low far from the expectation simply extrapolated using the data of pressure experiments on K<sub>3</sub>C<sub>60</sub> and Rb<sub>3</sub>C<sub>60</sub> in the BCS framework. Their  $T_c$ 's should be around 8-10 K. The other is the saturation in  $T_c$  for A<sub>3</sub>C<sub>60</sub> with large lattice parameters. The slightly higher  $T_c$  could be expected than the  $T_c$  values of Rb<sub>2</sub>CsC<sub>60</sub> ( $T_c = 31$  K) and RbCs<sub>2</sub>C<sub>60</sub> ( $T_c = 33$  K) considering their lattice parameters. Finally, both Li<sub>2</sub>CsC<sub>60</sub> and Li<sub>2</sub>RbC<sub>60</sub> are not superconducting, despite the apparent band filling by electron transfer into C<sub>60</sub> 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<sub>60</sub> molecular t<sub>1g</sub> 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<sub>60</sub> 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<sub>60</sub> 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<sub>60</sub>, 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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