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Superconductivity of Fullerenes: A Review.

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ABSTRACT

Fullerenes were discovered by Curl , Kroto and Smalley in 1985. C60 fullerene molecule composed of 20 hexagons and 12 pentagons has diameter of 0.7 nanometers. The C60 fullerene has a face centered cubic (fcc) lattice with a lattice constant of 14.17 °A at room temperature. Fullerene molecule is highly electronegative and form doped compounds with alkali metals. These doped fullerene molecules are superconductors at temperature below 20-40K. K_3C60 and Rb_3C60 shows superconductivity with the onset Tc of 18K and 28K. Not only potassium and rubidium doped superconductors have M_3C60 stoichiometry, indeed all the alkali-doped superconductors have same M_3C60 stoichiometry. However, Tc increases from 17 to 28 with increase in x from zero to 1 in Ki-xRbx (x= Rb to K ratio). Interestingly Rb_3C60 has a critical temperature of 27 K. Under strong pressure Cs_3C60 cmpound Tc can even increase to 40K. Although at atmosphoric pressure Cs_3C60 compound is both insulating and magnetic. Recently hole doped fullerenes system $C60/CHBr_3$ has exhibited greatest critical temperature , Tc = 117 K at ambient pressure for an organic superconductor. Field effect doping techniques have been expoited to prepare superconducting fullrenes. The maximum Tc of 52 K for 3±3.5 hole per C60 , which is almost five time higher than for electron doping has been absorved. Instead of preparing the superconductor in powered form fullerene nanowhisker (KxC60NWs) by potassium interaction has been prepared. In the present article a review of superconductive fullerenes derivatives is described.

Keywords: C60 fullerene, Superconductivity, alkali-doped fullerenes, hole doped fullerenes, Field effect doped fullrenes, fullerene nanowhiskers.

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INTRODUCTION

Metals are used for electricity transmission, but energy is lost as heat because of electrical resistance. Superconductors show no electrical resistance and can carry electricity without losing energy. Therefore, it is important to develop a superconductors which can work at ambient temperature. Most superconductors have simple structures built from atoms. But in recently, made superconductors molecules are arranged in regular solid structures. Among the different new materials with high temperature superconductivity, fullerene compounds are significant. Fullerenes are hollow-shaped carbon molecular aggregates. The simplest and most symmetric of which is the C60 molecule composed of 20 hexagons and 12 pentagons, as on a football. Discovered in 1985 by Curl, Kroto and Smalley [1] this molecule has a diameter of 0.7 nanometres. The C60 molecules have the form of a truncated icosahedron with *I*h point-group symmetry [2] (Figure-1) . Fleming *et al*. [3] first determined that after precipitation from solution the solid C60 crystallizes in the correct fcc structure [3, 4] (Figure 2) . However, it must be observed that, since the local symmetry is icosahedral, the full symmetry cannot be preserved in a crystal. A common structure that can accommodate a lower local symmetry is the bcc space group *Im*3. The reason for C60 choosing fcc over bcc has been suggested to be that the crystal chooses the highest density. It is not fully clear why the fcc structure is chosen over the hcp structure, which has the same density. It seems that in the presence of orientational distortion the fcc structure corresponds to a lower energy [4].
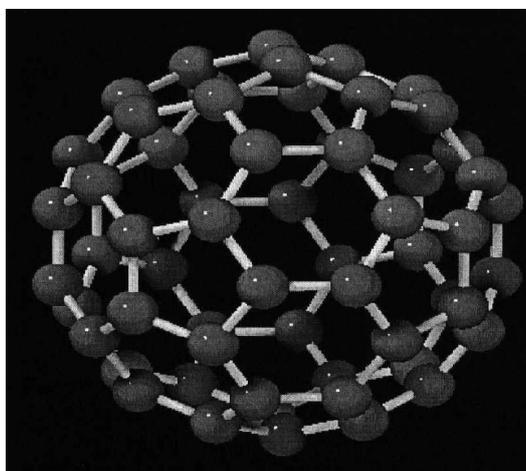
Figure-1: The structure of the C60 molecules [Rao , CNR , Seshadri , R , Govindaraj , A and Sen , R., 1995, Mater. Sci. Engng. 15, 209.]
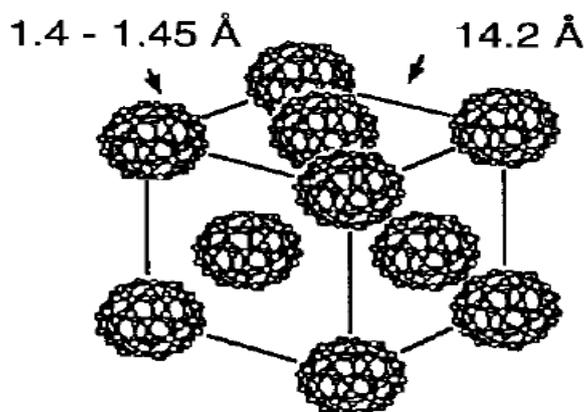
Figure-2: C60 in fcc structure with bond lengths [Leonardo Degiorgi, Fullerenes and Carbon derivatives from insulators to Superconductors, Advances in Physics , 1998, Vol-47, 207-316]

On the basis of extensive structural studies , it is now well established that solid C60 forms , a face – centred cubic (fcc) lattice with a lattice constant of 14.17 A° at room temperature [5-12]. In this structure the distance between nearest neighbor C60   cluster is 10 A° and thus the intercluster separation (diameter of C60= 7.1 A°) is 2.9 A°. This intercluster separation is .45 A° leas than 3.35 A ° interplanar separation in graphite . In addition , there are sizable empty holes , which constitute 26% of the total cell volume , within the fcc C60 lattice. There are two tetrahedral holes and one octahedral hole with radii of 1.12 A° and 2.06 A° respectively per C60 molecules [13] (Figure- 3).
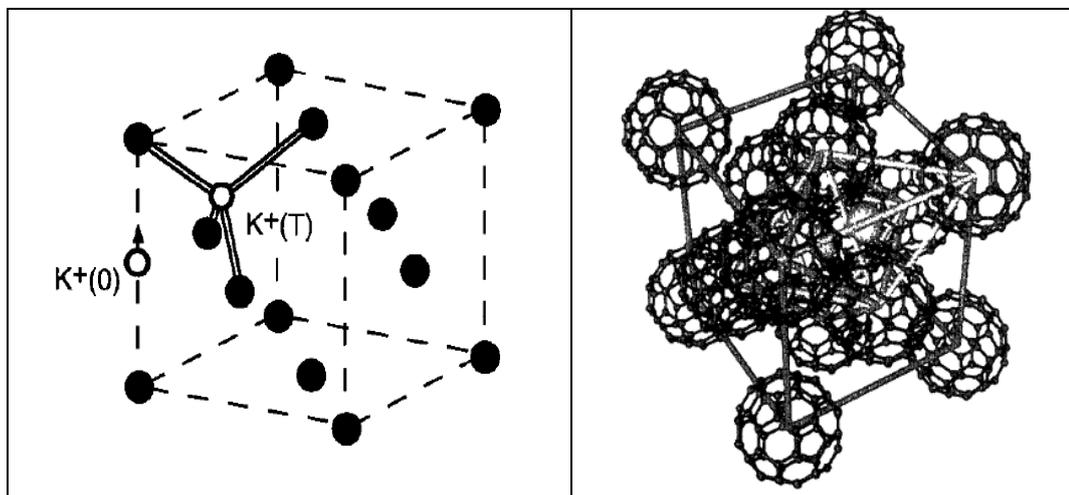
Figure –3a&3b: fcc lattice structure of solid C60 (solid O) showing the tetrahedral (K(T) and octahedral (K(O) alkali sites. The K (T) : K(O) site ratio is 2:1 [Zhang , F.C., Ogata, M., and Rice T.M., 1991 , Phys. Rev. Lett., 67, 3452]

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_iC60) in which all O-sites are singly occupied; (ii) the anti-fluorite type (A_2C60) in which all T-sites are occupied (iii) A_3C60 where all the T- and O-sites are occupied; and (iv) A_iC60 with half of the T-sites are selectively occupied (this has only been observed in the metastable Na_iC60). Most of the superconducting alkali metal fullerides have the same chemical composition of A_3C60 (A = A_i and Rb) and the face-centered cubic (fcc) structure, at least at room temperature. Two exceptions are the Cs_3C60 [14] and the NH_3K_3C60 [15] .Both have non-fcc structure and are only superconducting under hydrostatic pressure. In these compounds the charge transfer from alkali metal to C60 is almost complete, resulting a nearly triply minus-charged C60 molecule. This is due to the low ionization energy of A and the relatively large electron affinity of C60 [16, 17].

As fullerene molecule is highly electronegative, it readily forms compounds with electron donating atoms, the most common examples being alkali metals [34]. This reaction leads to production of an interesting class of compounds known as alkali-doped fullerides, wherein alkali metal atoms fill in the space between Buckyballs and donate valence electron to the neighbouring C60 molecule. If alkali atoms are potassium or rubidium, the compounds are superconductors, and they conduct electric current without any resistance at temperatures below 20-40 K [18], e.g., K_3C_{60} , Rb_3C_{60} . X-ray diffraction studies show that the alkali-doped fullerene has the same structure as C_{60} with fcc symmetry and the lattice parameter of the alkali- doped fullerene is smaller than that of C_{60} due to the coulomb interaction between alkali cations and C_{60} anions. Alternating current susceptibility and microwave absorption measurements confirm that K_3C_{60} and Rb_3C_{60} are superconducting with the onset T_c of 18K and 28K, respectively. The microwave absorption hysteresis measurements give an evidence of existing superconducting phase with the onset T_c of about 26K in the potassium-doped fullerene (Figure-4 and 5).

Although nethier the stoichiometry nor structure of the superconducting phase was known initially,but it was proposed that potassium intercalated into the octahedral and /or tetrahedral holes in the lattice. Subseqently studies have shown that the stoichiometries of the potassium [19, 20] and rubidium –

doped [20-22] C60 superconductors are K$_3$C60 and Rb$_3$C60, respectively. Indeed, all the known alkali metal – doped superconductors have the same M$_3$C60 stoichiometry (Figure-4&5). Lattice constants and transition temperature of the alkali metal –Doped C60 superconductors   are collected in Table-1 [23, 24]. A plot of Tc versus the Rb:K ration x in (Ki-xRbx) C60 shown in Figure-6 shows that Tc increases from 17 to 28 K with increase in X from zero to 1. The fcc lattice constant also increases from 14.253 to 14.436 as x increases from 0 to 1.   Figure-7 shows the variation in the superconducting transition temperature Tc with fcc lattice parameter *ao* for various composition of A$_3$C60 [22].
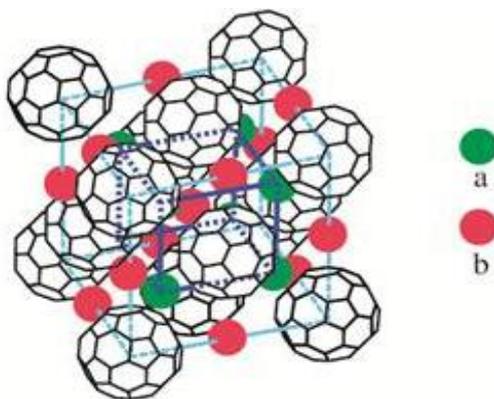
Figure-4: Model illustrating the packing of alkali metal ions into the tetrahedral and octahedral holes in the fcc M$_3$C60 lattice (left). The cluster are representated by gray shaded spheres and the alkali metal ions by smaller , light gray shaded spheres. [Yoshihiro Iwasa , Superconductivity: Revelations of the fullerenes,Nature , 466,191–192,(08 July 2010),doi:10.1038/466191a]
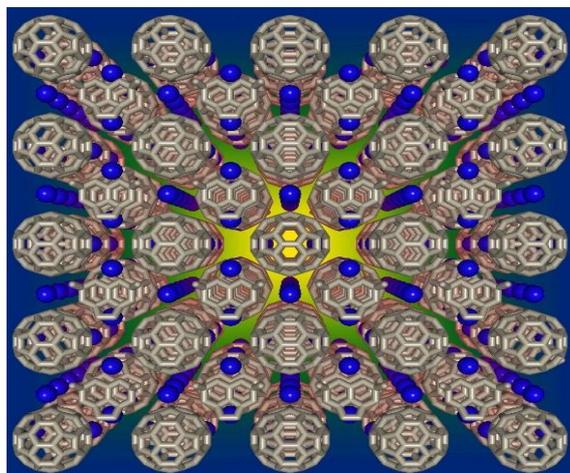
Figure-5: The fullerene molecules consist of 60 carbon atoms arranged in a truncated icosahedral shape (a soccer ball) and pack in a regular cubic-close-packed array in three dimensions. Alkali metal ions. [Ruth H. Zadik, et.al."Optimized Unconventional Superconductivity in a Molecular Jahn-Teller Metal", Science Advances, vol. 1, article number: e1500059, 2015]

Table-1: Lattice constants and transition temperature of the alkali metal–Doped C60 superconductors [Charles M. Lieber and Zhe Zhang , Physical Properties of Metal Doped Fullerene Superconductors ,Solid State Physics , Vol 48, 1994, 349-384, 23]

Material	FCC Lattice Constant (A°)	T_c (K)
Na_2RbC60	14.028	2.5
Na_2CsC60	14.133	11
K_3C60	14.253	19.2
K_2RbC60	14.299	21.8
K_2CsC60	14.292	24
KRb_2C60	14.364	26
Rb_3C60	14.436	29.4
$(NH_3)_4 Na_2CsC60$	14.473	29.6
Rb_2CsC60	14.493	31.3
Cs3C60	[A15, (bct lattice)]	40 – Pressure)(Pex 15 Kbar
$C60/CHCl_3$hole dopedand intercalated	117	
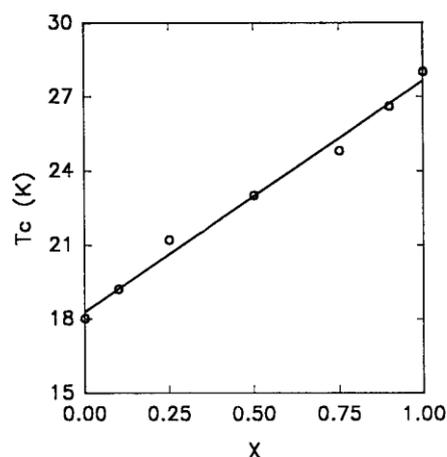
Figure-6: Plot of Tc versus the Rb: K ration x in (K i-xRbx) C60. The fcc lattice constant increases from 14.253 to 14.436 as x increases from 0 to 1] .
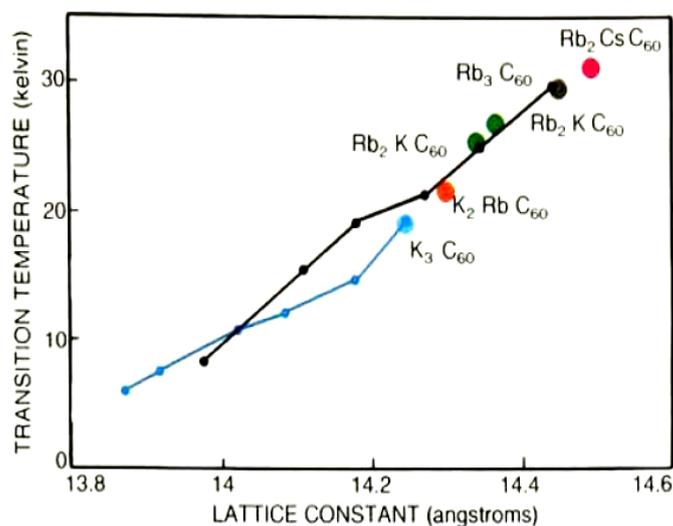
Figure-7: Tc of bulk samples of A3-x A'xC60 where A and A' represent K, Rb or Cs has nearly linear dependence on lattice constant a. Alkali atoms with larger ionic radii produce a greater effective negative pressure and large lattice constant. The lattice constants refer to fcc . Application of pressure causes a lattice contraction and corresponding decrease in Tc . Results determined for potassium and rubidium –doped C60 (blue and black lines , respectively) overlap with the zero pressure data ,Fleming R. M., et.al, 1991, Nature, 352, 787 , See O. et.al/, Science 255, 833 (1992), [36] Arthur F. H, Superconductivity in doped fullerenes, Physics Today November, 1992 , 26-32]

The one molecule composed of 3 alkalines for one fullerene is superconducting. For instance, Rb_3C60 has a critical temperature Tc of 27 K (-246°C). If a strong pressure is applied to the compound Cs_3C60, the Tc can even increase to 40 K. The molecular structure of this compound gives it significant superconducting properties. Now it is accepted that the interaction responsible for the electron pairing is located on the ball and was caused by the vibration modes of the ball. In order to try and increase the Tc, attempts to insert Cs (the biggest alkaline ion) were made, but it was only in 2008 that the synthesis of Cs_3C60 compounds was achieved [32]. The most surprising part was that the space between C60 was so big that the electrons were pinned to the balls and prevented them from relocating. At atmospheric pressure, the Cs_3C60 compound was hence both insulating and magnetic (Figure-8).
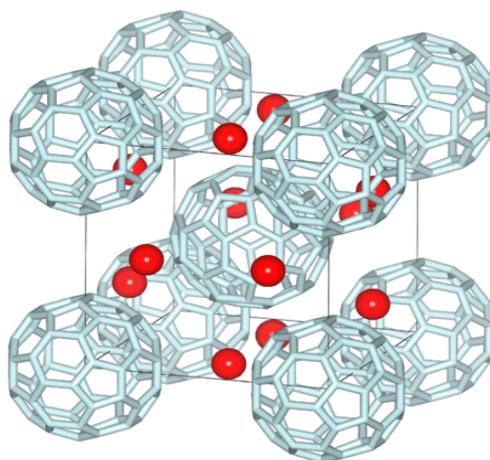
Figure–8: Structure of new fullerene compound Cs_3C_{60}. [The grey spheres in the shape of a soccer ball indicate fullerene molecules. The red spheres indicate cesium atoms. The distance between adjacent fullerene molecules is approximately 1 nanometer (one-billionth of a meter), [Yoshihiro Iwasa , Superconductivity: Revelations of the fullerenes,Nature , 466,191–192,(08 July 2010),doi:10.1038/466191a]

However, under a stronger pressure, the compound becomes a superconducting metal with a maximum Tc of 35 K (-238°C). This transition from an insulator to a metal (Mott transition) reminds of what happens in cuprates, pnictides, and heavy fermion compounds. When pressure is applied to the fullerene, the intermolecular distance is shortened, the electrons start moving, and the fullerene is transformed into a metal and exhibits superconductivity. The superconductivity of this fullerene with a high T_c is related to its electrical properties, which enable its transformation from an insulator to a metal(Figure-9).
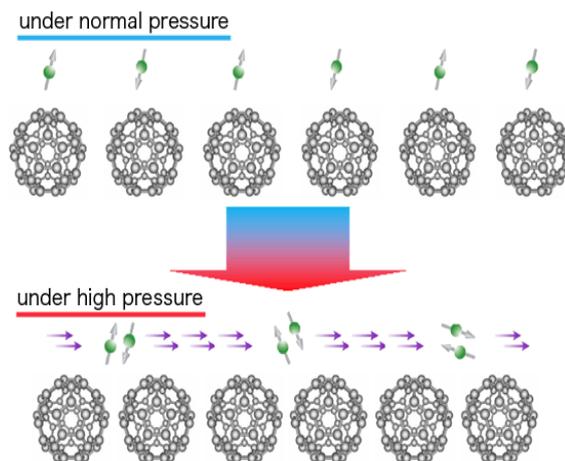
Figure-9: Change in electronic state of Cs_3C_{60} with respect to pressure clarified in this experiment [Yoshihiro Iwasa , Superconductivity: Revelations of the fullerenes,Nature , 466,191–192,(08 July 2010),doi:10.1038/466191a]

Hole doped fullerenes exhibit higher critical temperature than electron doped fullerenes [25]. Recently, Schoen et al. found a hole-doped C60 superconducting system C60/CHBr₃, which exhibited very high critical temperature Tc = 117K at ambient pressure. It is the greatest Tc for an organic superconductor with a buckyball doped with holes and intercalated with CHBr₃ [26] (Figure-10). Schoen expected that when bromoform or chloroform molecules are inserted inside a fullerene compound, they would sit in between the fullerene molecules. In this way, the fullerene molecules would be pushed apart similarly in the three directions. But, Dinnebier explained that the fullerene compounds with chloroform or bromoform were no longer cubic. Instead, the fullerene molecules form six-sided hexagonal shapes(Figure-10). The compound is made of parallel planes, each containing a series of connected hexagons. The chloroform and bromoform molecules sit in between the planes, pushing the fullerene molecules apart only in the direction perpendicular to the planes [27, 28]. While these results give a clearer picture of how a fullerene compound can be modified by adding chloroform or bromoform, but still it is not clear to what causes the increase of the superconducting temperature. One possibility is that when chloroform or bromoform molecules are added to the fullerene compound, their electrons add to the ones already existing in the compound. The collective motion of all the electrons then creates heat that increases the temperature. According to the theory, the number of electrons would have to increase by 25 to 35 percent to explain the measured superconducting temperature. However, Olle Gunnarsson, showed that, in a hexagonal structure, the number of electrons increases by, at most, 10 percent. Dinnebier has also suggested that the chloroform and bromoform molecules may play a role through interactions between their electrons, but this hypothesis has not yet been tested [27].
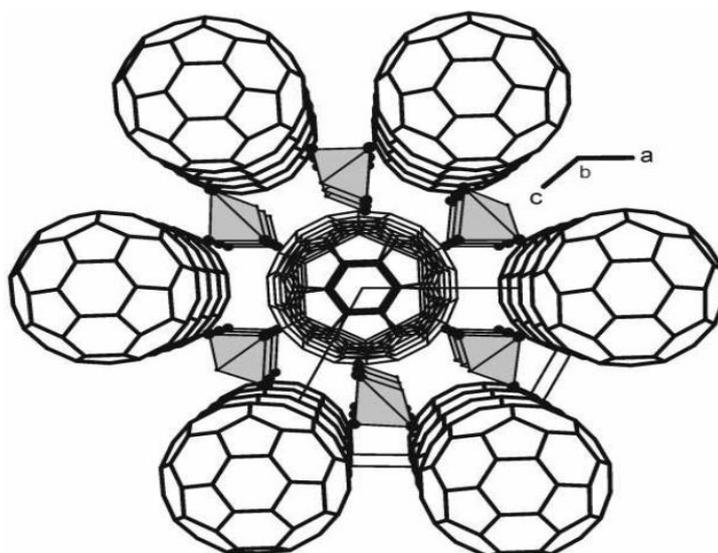
Figure-10: Structure of a fullerene crystal with chloroform molecules inserted within the lattice. Crystal structure of low phase of C₆₀.2CHCl₃ at T=50 K (Isotopic to C₆₀.2CHBr₃)in a view along b axis showing the close relation to the hexagonal room temperature phase. [Robert E. Dinnebier, et al., .Structure of Haloform Intercalated C60 and Its Influence on Superconductive Properties,. *Science*, 296, 109 (2002)].

Another technique, field-effect doping exploits the fact that under a strong, static electric field, charge (electrons or holes) will accumulate at the surface of the material, effectively modifying the electronic density in that region. This type of doping avoids imperfections that cause the system to deviate locally [29]. Schole et.al. in gate-induced superconductivity in hole- and electron-doped C60 single-crystal field-effect transistor structures have been able to sweep the charge carrier density continuously from, 4.5 holes per C60 to ,4.5 electrons per C60. The maximum Tc of 52 K for 3±3.5 holes per C60, which is almost five times higher than for electron-doping in the same geometry (11 K) [29, 30] was absorbed.

In general, superconducting K₃C60 bulk samples have been synthesized mainly by three methods, *i.e.*, a solid-solid reaction, vapor evaporation, and a reaction using liquids. Much effort has been expended to produce the K₃C60 superconductor, but a large volume fraction was difficult to obtain by a simple heating method. In addition, the obtained bulk superconductors of K₃C60 by the above methods were usually in

powder form. The above two were the problems inherent in the bulk application of K_3C60 superconductors. Keeping this in view, Takeya, et.al has synthesized superconducting fullerene nanowhiskers (C60NWs) by potassium (K) intercalation [31]. They showed large superconducting volume fractions, as high as 80%. The superconducting transition temperature at 17 K was independent of the K content (x) in the range between 1.6 and 6.0 in K-doped C60 nanowhiskers (KxC60NWs), while the superconducting volume fractions changed with x. The highest shielding fraction of a full shielding volume was observed in the material of K3.3C60NW by heating at 200 °C. On the other hand, that of a K-doped fullerene (K-C60) crystal was less than 1%.

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