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Electronic structure, conductivity and superconductivity of alkali metal doped C_{60}

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Abstract

The curvature and topology required for fullerene formation strongly enhances the electronegativity of the carbon clusters and as a result C_{60} readily accepts electrons. Solid C_{60} undergoes doping with alkali metal vapors to produce intercalation compounds which are conductors.During the doping process the predominant phases present are: C_{60}, A_3C_{60} and A_6C_{60}. The A_3C_{60} compounds are formed from C_{60} by occupancy of the interstitial sites of the fcc lattice.These phases constitute the first three-dimensional organic conductors and for A = K, Rb, the A_3C_{60} compounds are superconductors.

INTRODUCTION

Organic conductors depend on the presence of π-electrons for their electronic transport properties. In extended systems such as polymers and graphite, the π-system directly provides a conducting pathway, whereas in molecular systems[1] the transport properties depend on the overlap between the π-orbitals on adjacent molecules. The nature of the overlap is a crucial feature of the properties of molecular conductors, and the directionality of the π-orbitals exerts a profound effect on the resultant electronic properties. This constraint is in fact not imposed by the π-orbitals themselves, but by the planarity of the molecular framework which is usually thought necessary for delocalized π-bonding. However, there have been a number of molecules in the literature for some time that show marked nonplanarity and which are clearly aromatic.[2]

FULLERENES

With the observation[3] and synthesis[4] of the fullerenes this point became irresistible. The availability of these systems provided a set of molecules with π-orbitals radiating in all directions - if ever a 3-dimensional electronic molecular solid could be realized, then these molecules represented the ideal vehicle. The large size and high electron affinity[5] of the fullerenes provided a means to test this approach. By choosing a small dopant ion we reasoned that it should be possible to intercalate the fullerene crystal without disrupting the network of contacts between the spheroids and thereby generate the first 3-D isotropic organic conductor.[6] The FCC lattice[7] of C_{60} provides 3 interstitial sites per molecule, two tetrahedral and one octahedral, that are of sufficient size to be occupied by alkali metal cations.[6]

CONDUCTIVITY

These considerations led us to attempt the alkali metal doping of thin films of C_{60} and C_{70}.[6] We discovered that the conductivity of films of C_{60} and C_{70} increase by many orders of magnitude on doping with alkali metals. On prolonged doping the films became insulating. As electrons are added to the C_{60} molecules, they enter a conduction band composed of the triply degenerate t_{1u} π-orbitals of the individual fullerene molecules in the lattice. At half-filling (C_{60}^{3-}), maximum conductivity is observed; when the band is full (C_{60}^{6-}), the solid is again an insulator.[6]

SUPERCONDUCTIVITY IN K_3C_{60} AND Rb_3C_{60}

The highest conductivities occur with thin films of C_{60} doped with potassium.[6] When this combination was examined with microwave loss experiments, superconductivity was observed, with an onset at 18K.[8] This result was confirmed by conductivity measurements on thin films (Figure) and magnetization measurements on bulk K_xC_{60} samples which showed a well defined Meissner effect.[9,10]

Microwave loss experiments on thin films of Rb_3C_{60} samples provided evidence for a superconducting onset at 26K,[8] whereas magnetization measurements on bulk samples showed a T_c of 28K.[11,12]

Subsequent experiments have confirmed A_3C_{60} as the composition of maximum conductivity, and shown that it is this stoichiometry which is superconducting in the case of A = K, Rb.[12] The structure of this phase is that derived form the FCC lattice of C_{60} by occupancy of the interstitial sites with alkali metal cations.[13] The A_6C_{60} composition is the insulating phase, and this is now known to adopt a BCC structure.[14] These results verify our original postulates regarding the lattice and electronic structure of the doped fullerides,[6] as the lowest unoccupied molecular orbital of C_{60} is triply degenerate, and will hold a maximum of 6 electrons.[5]

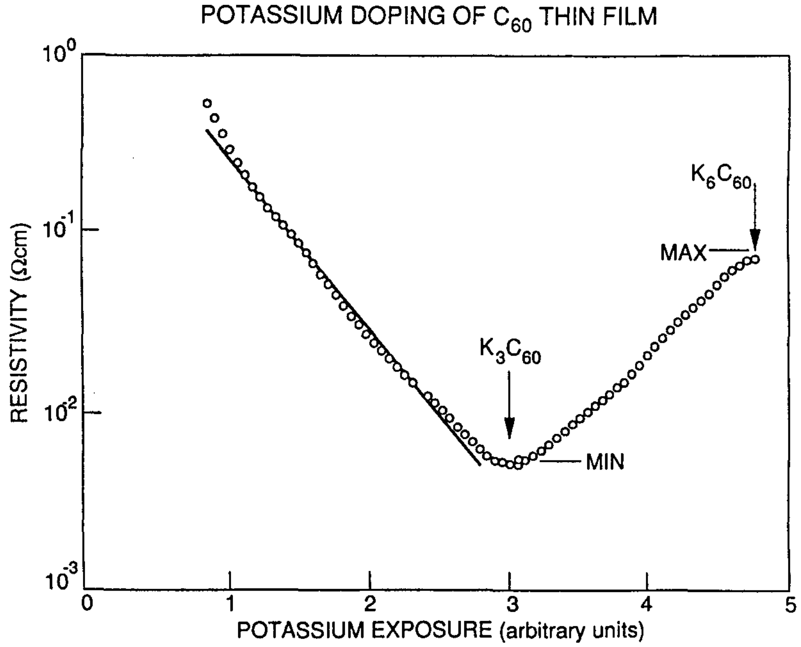

Figure. Resitivity of a K_xC_{60} film during exposure to a K molecular beam in UHV at ambient temperature near 74°C. The stoichimetries were determined by ex situ RBS analysis of a number of doped films.[15]

K_xC_{60} THIN FILMS

An experimental study of potassium doping of C_{60} films in UHV led to the resistivity profile shown in the Figure.[15] The available evidence suggests that the doped films consist of only three phases: C_{60}, A_3C_{60} and A_6C_{60}. When the film composition, K_xC_{60}, is $0>x>3$ the first two phases are present and when $3>x>6$ the latter two phases coexist in the film.[8,16-19] Thus the doping does not progress through K_1C_{60} and K_2C_{60} as would occur with a solid solution.[20] Only the film composition K_3C_{60} was found to be metallic, and the other compositions exhibited activated conductivity. This was interpreted in terms of the charging energy of the grains present in the C_{60} film. Films grown by sublimation consist of grains containing about 100 C_{60} molecules as X-ray diffraction experiments show random polycrystallinity with grain dimensions of about 60 Å.[21] It should be noted that the resistivity profile does not show the percolation threshold normally expected for a granular metallic system. Typically there is a marked change in the conductivity and temperature coefficient of resistivity at the percolation threshold which is expected to occur near a 50% volume fraction of the conducting phase. Thus the data in the Figure seem to require that the K_3C_{60} grains are determined by the preexisting grains in the films before doping. If the conducting regions are always located in the center of the grains, then the percolation threshold can be pushed arbitrarily close to the film composition $x=3$. As K_3C_{60} is the only conducting phase present, this surprising result requires that in the potassium poor region of the doping experiment ($0>x>3$), K_3C_{60} nucleates exclusively at the center of the grains and is always surrounded by outer layers of insulating C_{60}. Likewise in the potassium rich region ($3>x>6$), K_3C_{60} remains at the center of the grains, but becomes progressively separated from neighboring grains by the development of successive outer layers of insulating K_6C_{60} as the potassium concentration of the film increases. The latter result may be explained in terms of the change in structure which is required on progressing from the FCC C_{60} and K_3C_{60} to the BCC K_6C_{60} as it seems reasonable to expect that this process will occur from the outside of the grain and move inward. The former behavior would seem to require that K_3C_{60} is energetically more stable when surrounded by neutral C_{60}, perhaps because this allows completion of the coordination of the K^+ and C_{60}^{3-} ions in the lattice.

SUPERCONDUCTIVITY

Recent work by other laboratories has extended the class of alkali metal fullerides, and found materials with higher superconducting transition temperatures.[22,23] The dependence of T_c on the alkali metal intercalant may be accounted for by variations in the density of states at the Fermi level of these materials.[11,24-27] Recent theories of the superconductivity in the A_3C_{60} phases suggest that the electron-phonon coupling responsible for the superconductivity originates on the C_{60} molecule itself.[28-31] In this picture it is the intramolecular vibrations on C_{60}^{3-} which couple the conduction electrons into Cooper pairs which then are free to propagate through the lattice without resistive loss. These theories have received support from Raman and inelastic neutron measurements which show that the A_3C_{60} phase alone suffers a reduction in the number of observable peaks and that those peaks which remain are broadened.[19,32] These vibrations are missing or broadened because they scatter the conduction electrons and thereby provide the necessary electron-phonon coupling for BCS superconductivity. Additional support for the role of intramolecular C_{60} vibrations comes from ^{13}C isotopic substitution experiments and magnetization experiments.[33-35]

CONCLUSION

The alkali metal C_{60} superconductors suffer from their sensitivity to atmospheric moisture,[6] but show promising superconducting properties, including high critical magnetic fields.[36]

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