Electronic Structure, Conductivity, and Superconductivity of Alkali Metal Doped C_{60}

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This Account summarizes work carried out at AT&T Bell Laboratories on the fullerenes during the past few years. I begin with a discussion of the electronic structure of these molecules which was inferred from general theories soon after the fullerenes were identified by Kroto, Heath, O'Brien, Curl, and Smalley.[1] The high electron affinity[2,3] and the existence of radiating π-orbitals[4] when combined with simple ideas for the design of molecular metals and superconductors led us to pursue conductivity and superconductivity in the alkali metal doped fullerenes immediately after the synthesis of C_{60} and C_{70} by Krätschmer, Lamb, Fostiropoulos, and Huffman.[5] In the remainder of the Account I discuss the progress in the preparation and characterization of conducting and superconducting solids and films based on these materials and the current state of understanding which has been attained in this field.

The spheroidal geometry of the fullerenes is their most arresting feature, and it directly determines their singular electronic structure. As these molecules are solely composed of trivalent carbon atoms, the presence of a surface is implied, and given the fact that this valence state of carbon is best accommodated in six-membered rings (6-MRs), there is a tendency toward benzenoid structures. If the fullerenes were composed solely of conjugated 6-MRs, such as occurs in benzene and graphite, they would be alternant hydrocarbons (AHs).[6] Among the more important properties this classification confers is symmetry between the occupied and unoccupied molecular orbitals, that is, the bonding and antibonding HMO energy levels are symmetrically disposed about the energy zero.[6] Thus it is to be expected that benzenoid hydrocarbons and graphite will accept and donate electrons with equal ease. With appropriate adjustment of the reference potential, these compounds do exhibit mirror-image reduction and oxidation potentials.[7] Furthermore, polyacetylene and graphite (the infinite one- and two-dimensional AHs), undergo both n- and p-type doping in the solid state.[8]

The homologation of benzene rings produces a surface, and ultimately graphite, but with the inevitable dangling bonds due to the unsatisfied carbon valencies at the periphery of the sheet. The genius in the production of the fullerenes was the creation of an environment in which the formation of other structural possibilities was competitive with the generation of a purely benzenoid fragment with dangling bonds.[1,5] In order to remove the dangling bonds entirely, the edges of the surface must be eliminated, and this requires the

surface to close on itself: to produce a spheroid. The curvature imposed on the surface modifies the electronic structure of the sheet in two crucial ways, one of which relates to the electronic structure of the carbon atoms and the other to the bonding in the cluster.

The curvature of the surface at a carbon atom is most simply expressed by the pyramidalization angle $[(\theta_{\sigma\pi} - 90)°]$[2,4,9] shown in Figure 1. As the σ-bonds at a conjugated carbon atom deviate from planarity, the primary effect is a change in hybridization: a rehybridization of the carbon atom so that a π-orbital is no longer of purely p-orbital character and the σ-orbitals no longer contain all of the s-orbital character. Thus the fullerenes are of intermediate hybridization. Using the standard nomenclature, the σ-bond hybridization falls between the hybridizations of graphite (sp^2) and diamond (sp^3). An approximate treatment of the rehybridization required for closure of carbon spheroids of arbitrary size is shown in Figure 1. A recent analysis of ^{13}C NMR coupling constants in a derivative of C_{60} led to an estimate of 0.03 for the fractional rehybridization in neutral C_{60}.[10] The most important result for our purposes is the fact that the carbon 2s atomic orbital now mixes into the π-orbital, and because the 2s-orbital lies so much lower in energy than the 2p-orbital, the molecular orbitals which form from these rehybridized π-orbitals will have an enhanced electron affinity relative to the usual π-type molecular orbitals which result from pure carbon 2p atomic orbitals.

Apart from a curvature at the carbon atoms, closure of the sheet requires a modification of the benzenoid surface topology. Together with the 6-MRs, closure of the surface requires the presence of 12 5-MRs.[11] Conjugated 5-MRs, whether considered as radialenes,[12] cyclopentadienyls,[12] or pyracyclenes,[13] are always as-

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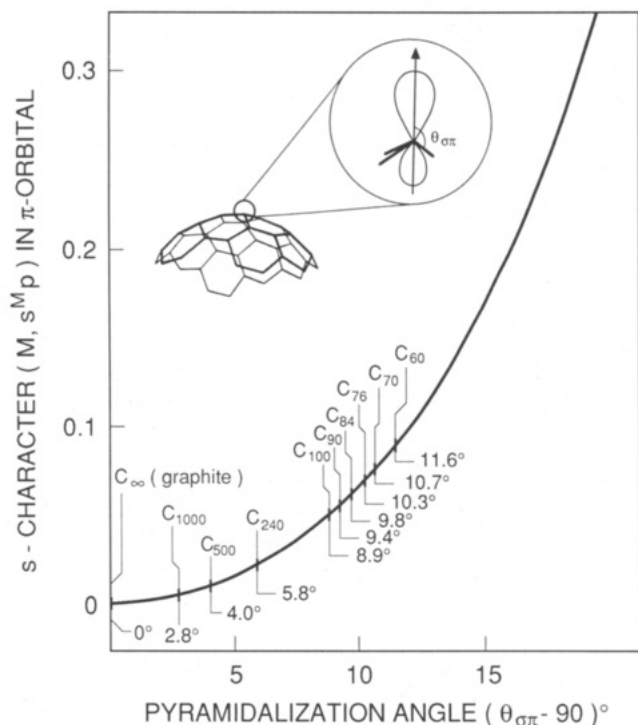
Figure 1. Rehybridization as a function of pyramidalization angle. The π-orbital axis vector (POAV1 approximation) is defined as that vector which makes equal angles to the three σ-bonds at a conjugated carbon atom.[4,9] The common angle to the three σ-bonds (which are assumed to lie along the internuclear axes) is denoted $\theta_{\sigma\pi}$. The average pyramidalization angle $[(\bar{\theta}_{\sigma\pi} - 90)°]$ shown for representative fullerenes was obtained from eq 2 of ref 2.

Figure 2. Hückel energy levels of C_{60} together with one component of the triply degenerate t_{1u} set of molecular orbitals which become populated on alkali-metal doping.

is more electronegative than any known hydrocarbon.

sociated with enhanced electron affinity as a result of the well-known stability of the cyclopentadienyl anion. The presence of the 12 5-MRs in the fullerenes guarantees that these molecules will all possess six low-lying energy levels. In the case of C_{60} the high symmetry leads to two sets of triply degenerate molecular orbitals (Figure 2).

Thus the two modifications which must be made in order to close the simple graphite sheet both bias the fullerenes toward an enhanced electron affinity. It is interesting to note that at large fullerene size both of these effects diminish in importance. The decreasing rehybridization is clear from Figure 1, and it is obvious that the effects of the 12 5-MRs will become diluted as the proportion of 6-MRs increases in the higher members of the series. Thus the larger fullerenes should begin to exhibit more symmetrical redox properties, although all fullerenes will possess at least six low-lying energy levels. It was on this basis that we predicted that C_{60} would exhibit an exceptionally high electron affinity and could accept up to 12 electrons under appropriate circumstances.[3]

The electron affinity has been measured as 2.65 eV,[14] and C_{60} is known to be able to accept two electrons in the gas phase.[15] Electrochemical studies have produced evidence for the reversible addition of up to five electrons to C_{60} in solution.[13,16] Thus it is clear that C_{60}
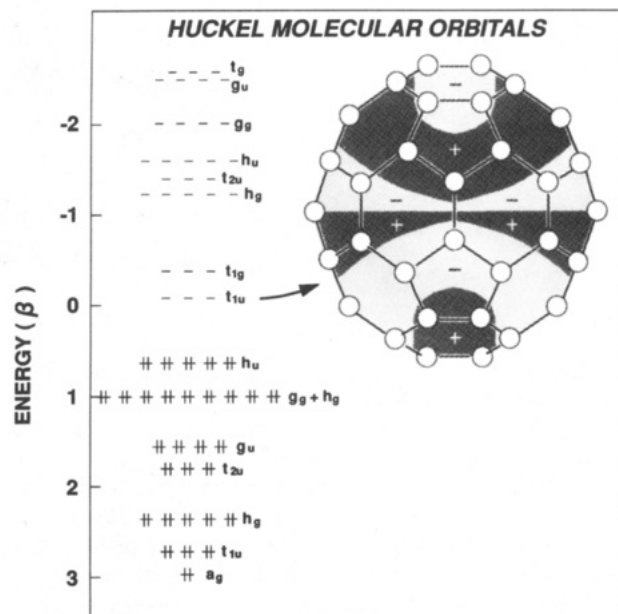
Design of a Molecular Metal and Superconductor

Although there has been much discussion of the possibilities for design of molecular electronic materials, most such new materials are limited by the availability of the constituent molecules. The availability of C_{60} presented a tremendous possibility to many branches of science: here was a totally new building block for the design of novel solid-state architectures and electronic materials. The shape was the most striking feature, and given the radiating π-orbitals, a three-dimensional electronic pathway was already present in the solid. All that was missing were the carriers, and from our understanding of the electronic structure, n-type doping (addition of electrons, as discussed above) seemed like the best direction. This approach would also allow the alkali-metal cations to fit into the lattice without disrupting the contacts between the C_{60} molecules necessary for overlap and electronic transport.

New classes of superconductors are rarely designed. Rather one seeks to obviate competing ground states, which are usually insulating. This point is well recognized in the case of organic charge-transfer compounds, which, as a result of their reduced dimensionality, are often subject to low-temperature transitions to charge or spin density wave ground states, thus eliminating the possibility of superconductivity. Hence the alkali fullerides were prime candidates for molecular superconductors, again, because of the shape of the fullerenes. Given the spheroidal electronic structure of C_{60} and the

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cubic crystal structure, an isotropic lattice was clearly favored. Thus, in a metallic solid dominated by the contacts between the C_{60} molecules, superconductivity seemed to be a viable candidate for the low-temperature ground state.

Discovery of the Alkali Metal Doped C_{60} Phases

The first experiments designed to produce alkali-metal fullerides were based on the electrocrystallization technique which had previously given rise to most of the superconducting TTF-derived charge-transfer salts.[17,18] In the TTF compounds, such as κ-ET$_2$Cu-(NCS)$_2$,[19] the organic component (ET) is oxidized at the anode, combines with a Cu(NCS)$_2^-$ counterion, and crystallizes on the electrode. Hence the conduction is realized with p-type doped molecules. As outlined above, it seemed best to attempt n-type doping of C_{60}; thus the molecule had to be reduced and paired with an alkali-metal counterion. The initial experiments were not promising, although Wudl and co-workers[20] were successful in isolating a charge-transfer salt containing reduced C_{60}. This material utilized a bulky counterion and was also found to contain supporting electrolyte in the lattice, which serves to inhibit contact between the C_{60} molecules and to limit the conductivity. These observations together with the tendency of C_{60} to crystallize from solution with other species in the lattice suggested that another route would be required which avoided the use of solvents. Subsequent work has shown that chemical reductions of C_{60} solutions are successful under certain conditions,[21] and reaction of C_{60} with the organic donor TDAE [tetrakis(dimethylamino)ethylene] has led to the synthesis of an organic ferromagnet.[22]

Films of C_{60} were described in the first report on the preparation of the fullerenes.[5] The availability of C_{60} thin films,[23] together with the fact that materials such as polyacetylene are frequently doped by vapor transport methods,[8] led us to devise an apparatus which would allow a similar experiment to be performed on the fullerenes (see Figure 3).[24] Films of C_{60} changed from yellow to magenta on exposure to alkali-metal vapor, and the conductivity increased by several orders of magnitude and then decreased. In situ Raman spectra of these doped films showed a softening of the high-frequency A_g vibration. We interpreted the mea-

surements in terms of the progressive filling of energy bands composed of the t_{1u} LUMO of C_{60} (Figure 2). At half-filling (C_{60}^{3-}) the conductivity reaches a maximum, and when the band is full (C_{60}^{6-}) the solid is once again insulating. When we turned our attention to the low-temperature properties of these alkali metal doped C_{60} phases ($A_x C_{60}$), we discovered superconductivity in the case of potassium (T_c = 18 K) and rubidium (T_c = 28 K) dopants.[25-27] Since this work was published, the preparation and properties of these materials have received a great deal of attention; in fact, Holczer et al.[28] and Wang et al.[21] reported superconductivity in Rb$_x$C$_{60}$ just a few days after our own submission on this phase. Thus it is already impossible to cover all contributions in the space of this Account.

Structure of the Alkali Metal Doped C_{60} Phases

In our initial model for conductivity in the doped C_{60} phases, we envisaged the introduction of the alkali-metal cations into the interstitial sites afforded by the lattice of C_{60} molecules.[24] This model is subject to two limitations: first, the contact between the C_{60} molecules is expected to be disrupted at a certain dopant size, which may weaken the overlap to the point that the material localizes or the lattice becomes unstable. Second, as C_{60} crystallizes in a face centered cubic (fcc) structure with one octahedral and two tetrahedral interstitial sites per C_{60}, the model could only account for compositions of $A_x C_{60}$, with x = 1–3.

Three distinct bulk phases have now been characterized: (a) the superconducting $A_3 C_{60}$ phase,[29] which retains the basic C_{60} fcc structure[30] with a slightly modified lattice constant; (b) the insulating $A_6 C_{60}$ phase,[31] which adopts a body centered cubic (bcc) structure; and (c) an intermediate composition $A_4 C_{60}$[32] of orthorhombic structure that is also insulating (Figure 4). The cubic symmetry of the $A_3 C_{60}$ compounds confirms the three-dimensional nature of the superconducting materials. It is now known that between x = 1 and 3, phase separation occurs for some intercalants and $A_1 C_{60}$ and $A_2 C_{60}$ disproportionate to neutral C_{60} and $A_3 C_{60}$.[33] In film-doping experiments conducted at room temperature, evidence has been adduced from Raman and microwave studies[27,34] for the occurrence

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Figure 3. Apparatus for measuring conductivities of doped fullerene films at low temperatures. The amber C_{60} film is on a glass substrate above an internal thermometer.

of $x = 0$, 3, and 6 (K, Rb) and $x = 0$ and 6 (Cs).

Electronic Structure of the Alkali Metal Doped C_{60} Phases

The important details of the electronic structure of the doped C_{60} phases may be inferred from the Hückel molecular orbitals of the isolated molecule (Figure 2). In the solid state the valence band derives from the C_{60} HOMO and the conduction band from the C_{60} LUMO. Extended Hückel theory (EHT) band structure calculations of the density of states (DOS) for C_{60} [simple

cubic (sc), $Pa\bar{3}$], C_{60} (fcc, $Fm\bar{3}$), K_3C_{60} (fcc), Rb_3C_{60} (fcc), K_4C_{60} (orthorhombic, $Immm$), and K_6C_{60} (bcc, $Im\bar{3}$) are shown in Figure 5. The bonding σ-orbitals lie too high in the EHT calculations by about 2 eV and obscure the π-orbitals which make up the valence band.[35] It is known from photoemission studies[36-39] and high-level

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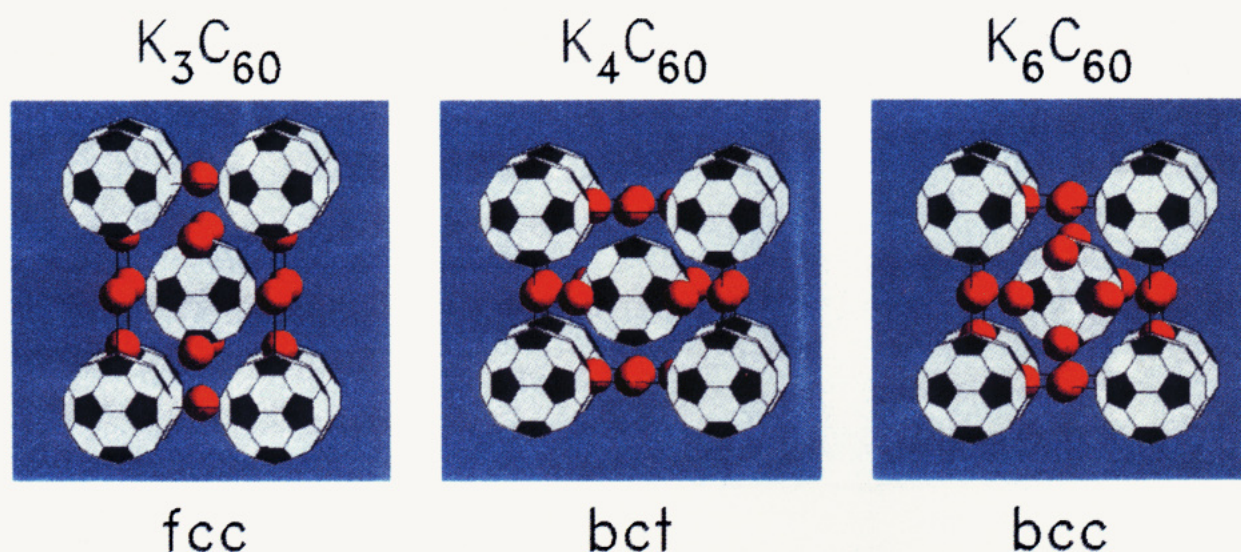
K$_3$C$_{60}$ K$_4$C$_{60}$ K$_6$C$_{60}$

fcc   bct   bcc

Figure 4. Structures of the alkali metal doped phases K$_x$C$_{60}$: (a) fcc K$_3$C$_{60}$, (b) bct K$_4$C$_{60}$, and (c) bcc K$_6$C$_{60}$.

band structure calculations[40,41] that the two highest lying bands in neutral C$_{60}$ originate from the molecular h$_u$ (g$_g$, h$_g$) π-levels (Figure 2).

The sc and fcc neutral C$_{60}$ structures differ only in the orientations of the C$_{60}$ molecules,[42–44] yet there is a clear effect on the DOS of the conduction band (Figure 5). Note that the expansion of the lattice between C$_{60}$ and K$_3$C$_{60}$ is relatively minor[29,45] and exerts a small effect on the calculated DOS. Within the simple orbital picture adopted in this discussion, which neglects nonrigid band effects,[37] the change in DOS along the series C$_{60}$, K$_3$C$_{60}$, and Rb$_3$C$_{60}$ is similar.

The main feature of the DOS calculations is the relative invariance of the t$_{1u}$- and t$_{1g}$-derived conduction bands. Although differences exist, the band widths and energy gaps remain qualitatively unchanged. Hence the molecular features of C$_{60}$ dominate the electronic structure of the solid phases. It is clear from Figure 5 that the A$_6$C$_{60}$ compounds will be insulators as the t$_{1u}$-derived band is filled at this doping level. The A$_4$C$_{60}$ phases appear to be metallic, but this is known not to be the case.[32] In the present theoretical treatment the C$_{60}$ molecular structure is taken from an MNDO optimization of the neutral molecule in I_h symmetry,[35] but the C$_{60}{}^{4-}$ ion may undergo a static Jahn–Teller distor-
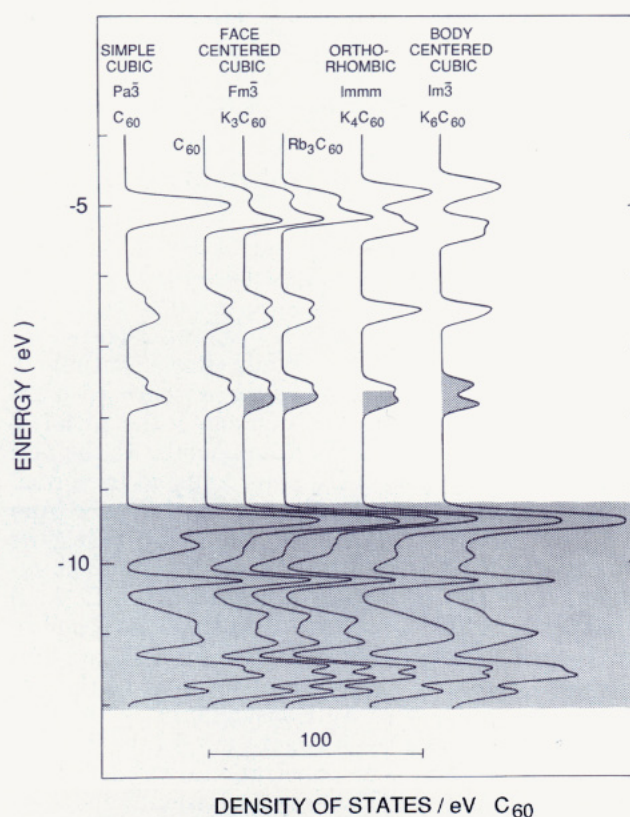

Figure 5. EHT density of states from band structure calculations on C$_{60}$ and its alkali metal doped phases.

tion,[46] perhaps driven by electron correlation effects,[37] leading to a gap in the DOS which would account for the insulating ground state. The A$_3$C$_{60}$ phases are not expected to be subject to a Jahn–Teller distortion,[46] and the metallic ground state survives.

The narrow band width, $\sim$0.5 eV, is about half that normally associated with organic conductors.[18] These band widths are determined by the intermolecular overlap of π-orbitals, but in the case of previous organic superconductors, these overlaps were dominated by

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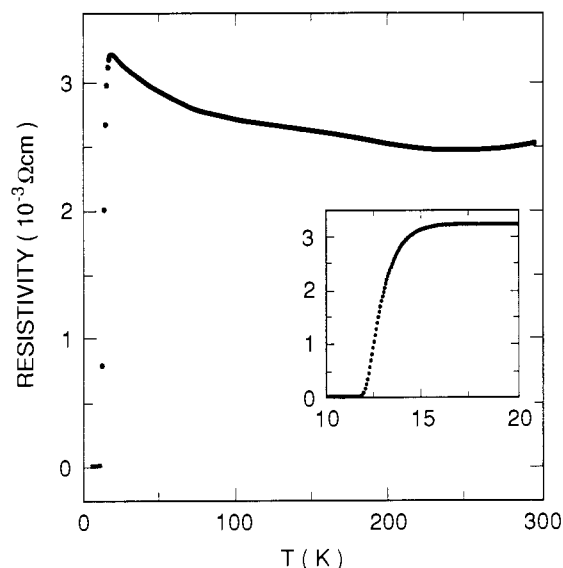
Figure 6. Temperature dependence of the resistivity of a thin film of K_3C_{60}.[51]

contributions from chalcogenide atoms, which are absent in the alkali fullerides. The narrow band width, together with the degeneracy of the molecular t_{1u} levels, results in a fairly high density of states at the Fermi level [$N(E_F)$].

Superconductivity of the Alkali Metal Doped C_{60} Phases

A number of distinct alkali metal doped C_{60} superconductors have now been prepared, with T_c values up to 33 K.[25-28,45,47,48] In addition, a superconducting transition temperature of 45 K has been reported for C_{60} codoped with Rb/Tl.[49] While efforts continue to synthesize new compositions, the absence of high-quality single crystals has hampered the physical characterization of the known compounds. In the case of alkali-metal doping of C_{60} films prepared by normal sublimation techniques,[5,23] there is now evidence from both normal[50] and superconducting[51] state transport measurements (Figure 6) that these are granular superconductors with a grain size of 60-70 Å. A high upper critical field ($H_{c2}(0)$ = 49 T) has been found in bulk magnetization measurements[52] on K_3C_{60} and interpreted in terms of a very short superconducting coherence length, ξ = 26 Å. Consideration of the film granularity implies a much larger value for the Pippard value, ξ = 150 Å.[51] The penetration depth has been measured as $\lambda(0)$ = 2400 Å (magnetization)[52] and 4800 Å (muon spin relaxation, μSR).[53] The μSR experiments find an isotropic superconducting energy gap without nodes or zero points (s-wave superconductivity).
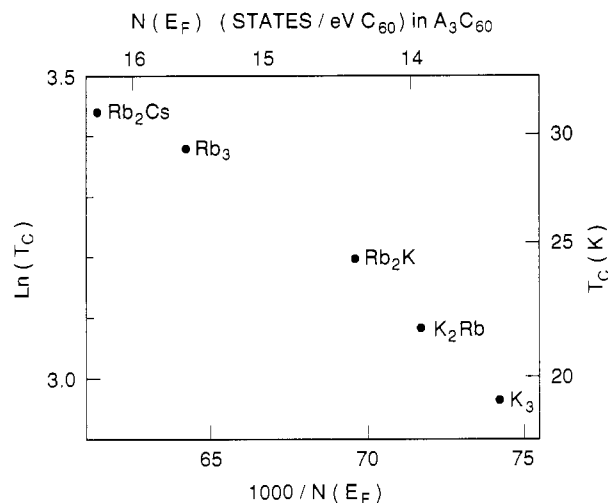

Figure 7. Plot of the natural logarithm of the superconducting transition temperature (T_c) against the reciprocal of the density of states at the Fermi level [$N(E_F)$], as calculated by EHT band structures.

Superconductivity requires the presence of an attractive interaction between pairs of electrons close to the Fermi level. In the weak coupling BCS model for phonon-mediated electron pairing, T_c is given by

$$T_c = \omega_{ph} e^{-1/VN(E_F)} \tag{1}$$

where ω_{ph} is the energy of the phonons and V is the electron–phonon coupling strength. In a study of a series of alkali metal doped C_{60} compounds, we found a functional dependence between the superconducting transition temperature (T_c) and the lattice constant, which was in turn related to the calculated density of states at the Fermi level [$N(E_F)$].[45] A plot of ln (T_c) vs $N(E_F)^{-1}$ for some representative compounds is shown in Figure 7. Linear behavior is in accord with eq 1 if the phonon frequencies and the electron–phonon coupling constants remain constant among the various A_3C_{60} compounds. The values derived from the calculations shown in Figure 7 are ω_{ph} = 300 K and V = 0.03 eV. Thus the values of T_c appear to be determined by the density of states at the Fermi level in these materials.[26,45,54] Studies of the A_3C_{60} superconductors under pressure also support this interpretation.[55]

A number of theories have been advanced to account for the superconductivity in the A_3C_{60} compounds. Although the above treatment is cast in terms of phonons, other pairing-mediating excitations could be involved, and alternative pairing schemes are receiving attention.[56,57] It has been argued that the intermolecular optic phonon modes (ω_{ph} ~ 160 K) couple strongly to carriers on C_{60}.[58] However, the idea that intramolecular vibrations on the C_{60} molecule are re-

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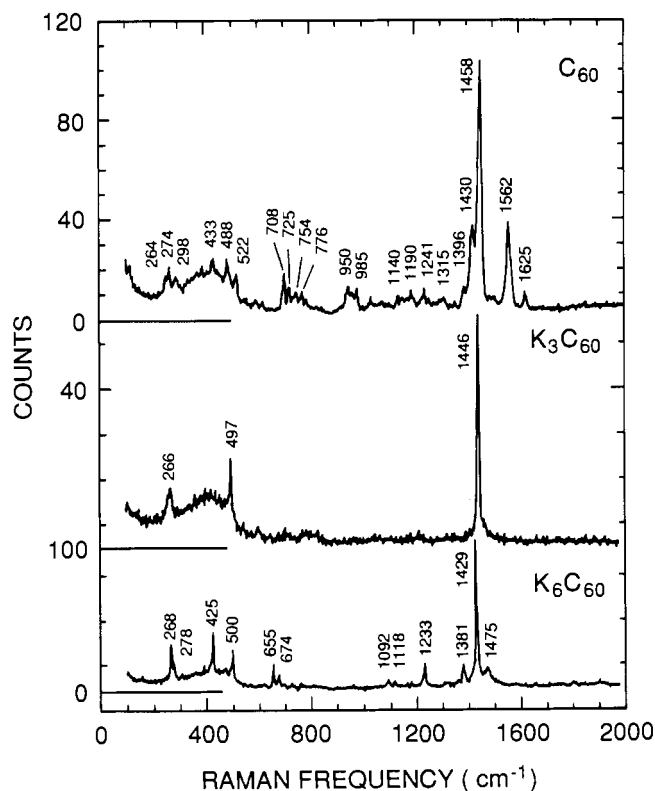
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Figure 8. In situ Raman spectra of a C$_{60}$ film taken during potassium doping: C$_{60}$, K$_3$C$_{60}$ (superconducting), and K$_6$C$_{60}$ (insulating).[34]

sponsible for the pairing has also received consideration.[26,45,46,59-61] These theories naturally account for the linearity shown in Figure 7 because the relevant phonons are expected to be independent of dopant. The elevated superconducting transition temperatures in the A$_3$C$_{60}$ compounds then result from the high-frequency intramolecular vibrations of the C$_{60}$ molecule. The phonon frequency obtained from Figure 7 is not expected to be reliable and must be considered as consistent with any of the above theories, at least in the case of the phonon mechanisms. The application of more sophisticated treatments of the superconductivity[54,62] considerably modifies the parameters derived from Figure 7 on the basis of eq 1. Furthermore, the interpretation of these materials within standard BCS theory has recently been called into question on the

basis of tunneling studies which suggest strong electron–phonon coupling.[63]

As shown in Figure 8, there is a marked decrease in the number of peaks seen in the Raman spectrum of K$_3$C$_{60}$ as compared to C$_{60}$ and K$_6$C$_{60}$.[34] Although this may be a reflection of the metallic character of the A$_3$C$_{60}$ phase, it could also result from the strong scattering of the electrons by these modes (predominantly H$_g$), which become broadened to the point that they are no longer observable.[46,61] In this latter interpretation, it is the intramolecular vibrations of the C$_{60}$ molecule which are missing from the Raman spectra of the A$_3$C$_{60}$ phases[34] that supply the electron–phonon coupling necessary for superconductivity in these materials.[46,61] A recent inelastic neutron scattering study of K$_3$C$_{60}$ also implicates the H$_g$ vibrational modes in the superconducting pairing mechanism.[64] Nevertheless, the implication of high-frequency intramolecular vibrations in the A$_3$C$_{60}$ superconductors calls into question the applicability of Migdal's theorem (Born–Oppenheimer approximation), as the phonon frequency is now comparable to the Fermi energy (~half the band width).[65]

Although the nature of the pairing mechanism in the A$_3$C$_{60}$ superconductors remains to be established, the simplicity of the materials and the progress already made suggest that a definitive resolution of this question may be achieved more quickly than in the case of the high-T_c copper oxide superconductors.

Concluding Remarks

In less than a year the singular shape and electronic structure of the fullerenes have been exploited to produce molecular conductors, superconductors, and ferromagnets. The opportunities afforded by this unique class of molecules is limited only by our imagination.

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