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ELECTRONIC PROPERTIES OF ORGANIC SUPERCONDUCTORS

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Abstract The electronic structure and metallic properties of the 3-D $A_3 C_{60}$ and 2-D κ-$ET_2Cu(NCS)_2$ organic superconductors are compared. It is conclude that both classes of materials are close to the metal-insulator transition. The mean free path in the $A_3 C_{60}$ metals is anomalously short, in comparison with that calculated for κ-$ET_2Cu(NCS)_2$.

The $A_3 C_{60}$ (A = K, Rb) phases are superconductors, with structures that are derived from the face-centered cubic (fcc) lattice of solid C_{60}, by population of the interstitial sites.[1] The three-dimensional (3-D) conduction band of these phases arises from the t_{1u} orbitals of the free molecule which hybridize together in the lattice to form a narrow band metal.

In Figures 1 and 2, the EHT calculated band dispersions (obtained by a straight-line fit to certain k points in the Brillouin zone), are shown for the t_{1u} - and t_{1g} - derived bands.[1-3] The Fermi levels in these calculations are found at $E_F(K_3C_{60})$ = -7.63 eV and $E_F(Rb_3C_{60})$ = -7.65 eV. If the ordinates of these plots are adjusted for this difference in the location of the Fermi level in these solids, then it is apparent that the upper bands of K_3C_{60} and Rb_3C_{60} are brought into almost exact coincidence. Thus the changes in electronic structure that accompany variations in lattice constant, $N(E_F)$, and T_c, arise solely from differences in the lower two bands which are occupied at certain points in the Brillouin zone.

The trend in the superconducting transition temperatures in the $A_3 C_{60}$ phases[4] is an inverse function of the density of states at the Fermi level [$N(E_F)$], and is reasonably well described by band structure calculations,[5,6] including those based on EHT theory.[1-3] Nevertheless a comparison of the band-structure-derived bare density of states at the Fermi level, with the $N(E_F)$ values derived from measurements of the normal state Pauli magnetic susceptibility for a variety of 1-D, 2-D and 3-D organic superconductors showed that the experimental values exhibit a strong enhancement, which was take as evidence of strong electron-electron correlations in these materials.[3] This is to be expected because estimates place the on-site Coulomb correlation energies in the range $U \approx 0.5$ - 2 eV - values that are large compared to estimates of the band width in these

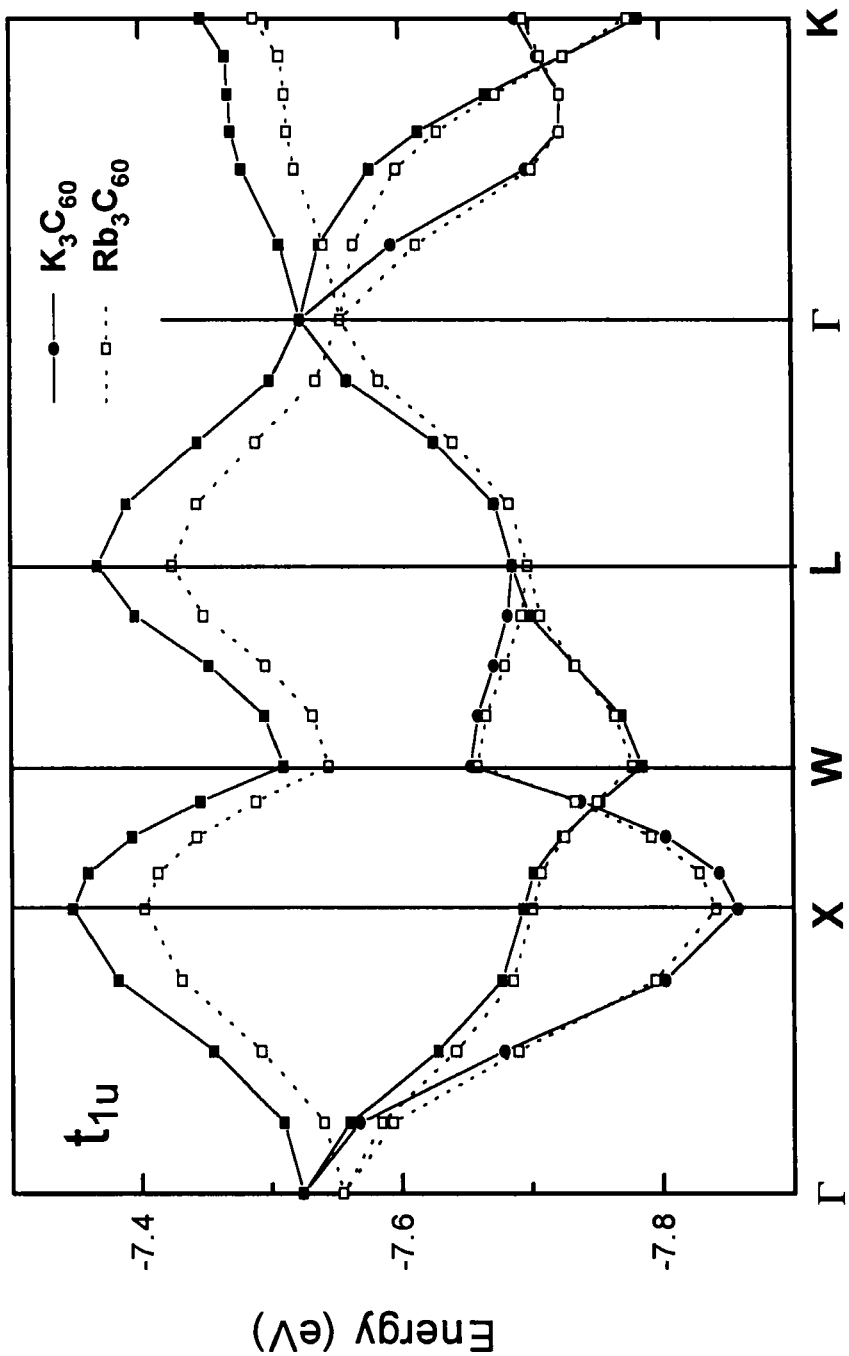

FIGURE 1. Electronic band structures calculated for the t_{1u} -derived bands of K_3C_{60} and Rb_3C_{60}.

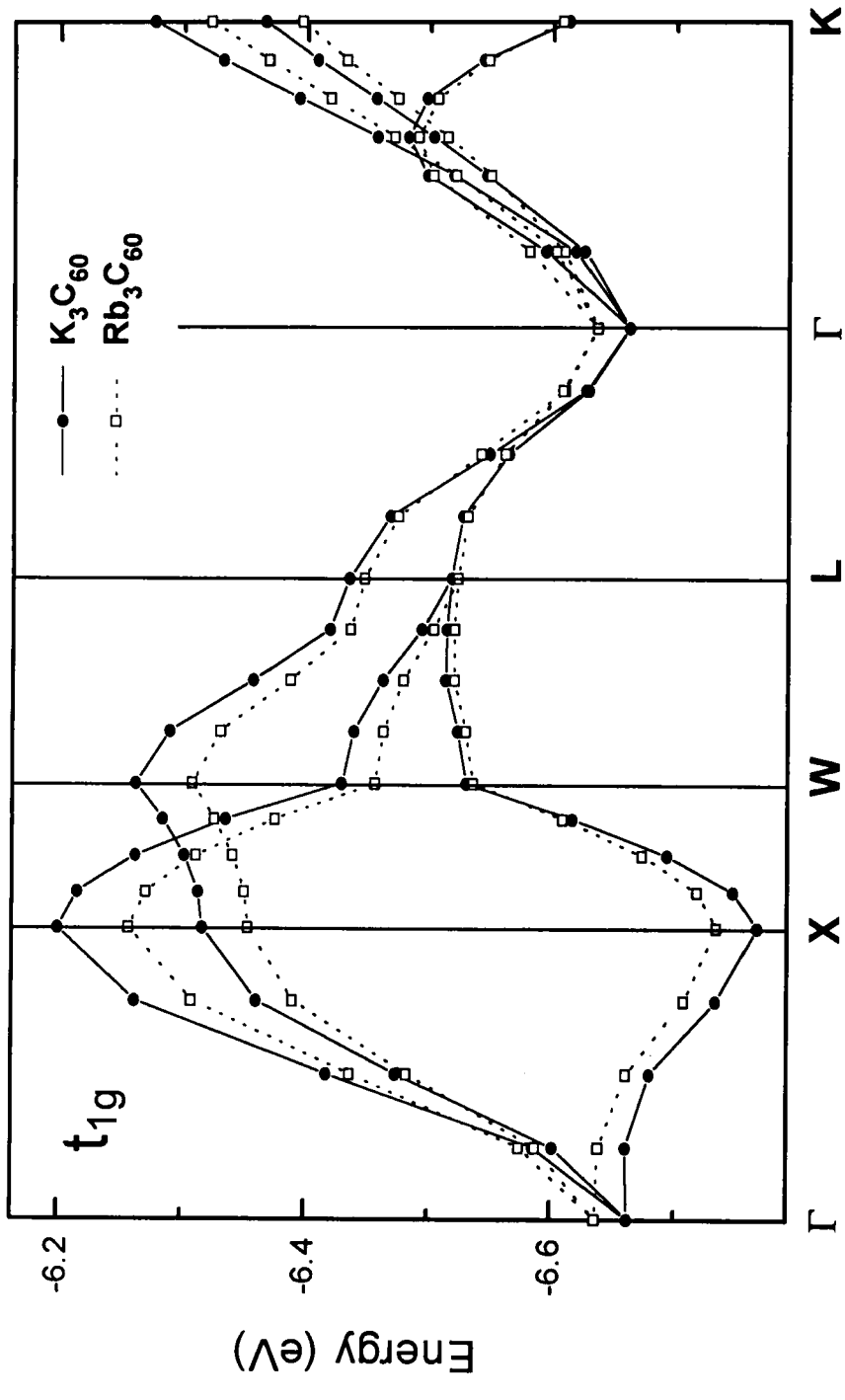

FIGURE 2. Electronic band structures calculated for the t_{1g} -derived bands of K_3C_{60} and Rb_3C_{60}.

salts which are in the range W ≈ 0.5 - 1 eV (The values of W in Fig.1 are 0.51 eV (t_{1u}), 0.57 (t_{1g}) and 0.44 (t_{1u}), 0.48 (t_{1g}) for K_3C_{60} and Rb_3C_{60}, respectively).

There are a number of outstanding problems that remain to be resolved regarding the electronic structure of the A_3 C_{60} superconductors and their metallic properties.[7,8] In this article we revisit the question of the normal state conductivity in these phases[8-10] and compare these compounds with the organic superconductors based on tetrathiafulvalene (TTF). As a representative of this latter group we choose κ-$ET_2Cu(NCS)_2$,[11] because this compound is one of the most carefully studied of the 2-D organic superconductors[12] and provides a useful point of comparison with the 3-D A_3C_{60} materials.

MOTT LIMIT IN ORGANIC SUPERCONDUCTORS

In order to compare the two classes of superconductors we use the free electron treatment. Although this model is extremely simple it allows the derivation of a variety of quantities of interest with regard to the normal state metallic properties of a wide range of compounds. A difficulty arises in the application of the free electron model to A_3 C_{60} metals because the conduction band in these solids is composed of the triply degenerate t_{1u} orbitals of the C_{60} molecule which contain three electrons. We have previously dealt with this complication within two different approximations.[8-10] In Case 1, the electronic structure is treated in terms of a single non-interacting conduction band. In this treatment the complications due to degeneracy are ignored and the normal free electron expressions evaluated. However, reference to Figure 1 shows that two of the bands actually cross along certain directions in the Brillouin zone. In Case 2, there are assumed to be three degenerate bands. In either case, the conduction electron density, $n = 4.1 \times 10^{21}$ cm^{-3} in the A_3 C_{60} metals.

Case 1. Fermi Wavevector (k_F) for Single Non-Interacting Band in A_3 C_{60}. In a simple 3-D metal with a spherical Fermi surface, the Fermi wave vector may be evaluated from the expression, $k_F^3 = 3\pi^2 n$; this gives rise to $k_F = 5.0 \times 10^7$ cm^{-1}.

Case 2. Fermi Wavevector (k_F) for Three Degenerate Bands in A_3 C_{60}. Now the volume enclosed by the Fermi surface is scaled by the degeneracy, and $k_F^3 = \pi^2 n$; thus $k_F = 3.4 \times 10^7$ cm^{-1}.

From a knowledge of the Fermi wavevector it is possible to derive the Mott limit (σ_{Mott})[13] in these materials, that is, to determine whether they qualify as normal Fermi liquids by a comparison of the experimentally observed limiting conductivity $\sigma(T = 0)$ with σ_{Mott}. This is an important issue because the low conductivities in many organic metals naturally raises this question.

We use the general relationship between the conductivity, the Fermi surface area (S_F) and assume an isotropic mean free path (l). For a 3-D metal $\sigma = (2\pi e^2/h)(12\pi^3)^{-1}$ (S_F l).

Case 1. Mott Limit (σ_{Mott}) for Single Non-Interacting Band in A_3C_{60}. For a metal with a spherical Fermi surface, the Fermi surface area is given by $S_F = 4\pi k_F^2 = 3.1 \times 10^{16}$ cm^2. The Mott limit is usually taken as $k_F l > 1/(2\pi)$. Physically, in atomic metals this corresponds to the condition that $l > a$, where a is the interatomic distance. By substituting $k_F l = 1/(2\pi)$, we evaluate the Mott limit for Fermi liquid behavior in these materials from the expression $\sigma = (2\pi e^2/h)(12\pi^3)^{-1}[4\pi k_F(k_F l)]$. Thus in this approximation, $\sigma_{Mott} = (2\pi e^2/h)(6\pi^3)^{-1} k_F = 70$ S/cm.

Case 2. Mott Limit (σ_{Mott}) for Three Degenerate Bands in A_3C_{60}. In order to allow for the degeneracy we take $S_F = 3 \times 4\pi k_F^2 = 4.4 \times 10^{16}$ cm^2. Thus by using the expression $\sigma = (2\pi e^2/h)(12\pi^3)^{-1}[12\pi k_F(k_F l)]$, and substituting $k_F l = 1/(2\pi)$, we obtain $\sigma_{Mott} = (2\pi e^2/h)(2\pi^3)^{-1} k_F = 140$ S/cm as the Mott limit for Fermi liquid behavior in these materials.

This analysis shows that the A_3C_{60} metals, in spite of their low conductivities, can be treated as normal Fermi liquids.[8-10] Nevertheless, they are quite close to the metal-insulator transition. Related M_xC_{60} phases do not show metallic behavior and probably qualify as Mott insulators, although these compositions have a different degree of band-filling.

UHV doping experiments on granular C_{60} thin films[14] gave conductivities at 333K of σ = 140 S/cm for Cs_1C_{60} and σ = 1 S/cm Cs_4C_{60}, both of which showed activated behavior. Of the alkali metals, only K_xC_{60} and Rb_xC_{60} with $x \approx 3$ and $\sigma >$ 200 S/cm showed a metallic temperature dependence. Similar experiments on Ca_xC_{60}, Sr_xC_{60} and Ba_xC_{60} thin films[15,16] detected metallic behavior only in the case of Ba_xC_{60} with $x \approx$ 4-6 and $\sigma >$ 250 S/cm. Thus metallic character is the exception in the case of the M_xC_{60} phases.

Mott Limit (σ_{Mott}) for κ-$ET_2Cu(NCS)_2$. This organic superconductor is known to be strongly 2-D, and its possesses an almost cylindrical Fermi surface.[12] In order to simplify the analysis, we make no allowance for the fact that two bands cross the Fermi level. We treat the system as a simple 2-D metal, and obtain a (sheet) carrier density, $n = 1.8 \times 10^{14}$ cm^{-2}. In this approximation the Fermi surface is a circle of radius the Fermi wavevector (k_F) and the Fermi surface area is given by $S_F = \pi k_F^2$. Hence $k_F^2 = 2\pi n$, and $k_F = 3.4 \times 10^7$ cm^{-1}. For a 2-D metal with an isotropic mean free path (l), $\sigma = (2\pi e^2/h)(8\pi^3)^{-1}(S_F l) = (2\pi e^2/h)(8\pi^3)^{-1}[\pi k_F(k_F l)]$. Taking $k_F l = 1/(2\pi)$, we obtain the Mott limit for Fermi liquid behavior in these materials as, $\sigma_{Mott} = (2\pi e^2/h)(16\pi^3)^{-1} k_F =$ 17 S/cm.

This is remarkably close to the room temperature conductivity of this material (although well below the low temperature limiting value). Oshima, *et al.*, report room temperature values of 14-20 S/cm and 24-40 S/cm along the b- and c-axes, respectively.[17] Gartner, *et al.*, report 20 S/cm for the in-plane conductivity,[18] and the high temperature part of the data corresponding to the results shown in Fig. 3[19] give a

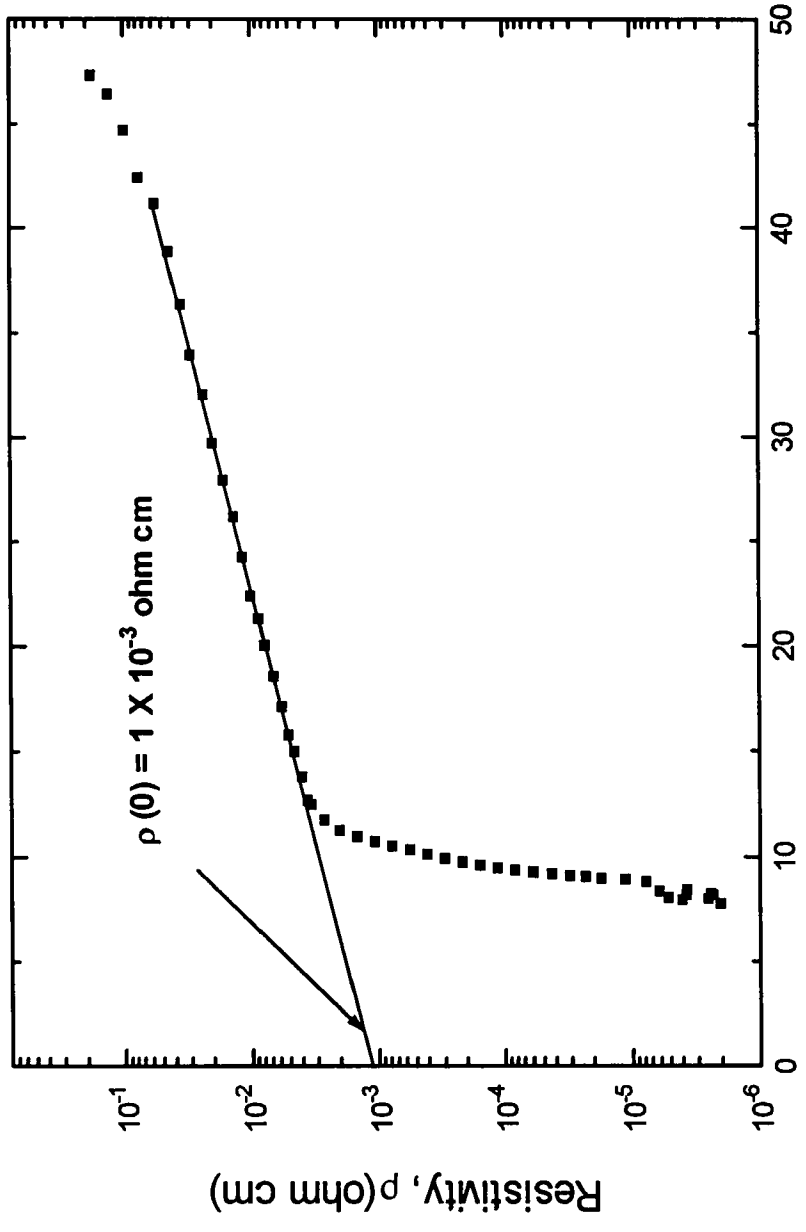

FIGURE 3.. Log-linear in-plane resistivity plot for κ-$ET_2Cu(NCS)_2$,[19] extrapolated to T = 0.

value of about 15 S/cm. It is interesting to note that the conductivity of this compound initially decreases, before beginning to increase at about 100K. Thus it is possible that the anomalous resistivity behavior is associated with the proximity of this material to a metal-insulator transition.

Thus there are strong electron-electron interactions in all of the organic conductors as a result of the fact that $U/W \approx 1$ in these materials.[3]

MEAN FREE PATH IN ORGANIC SUPERCONDUCTORS

Mean Free Path (l) in A_3C_{60}. We take as residual resistivity $\rho(0) = 1.2 \times 10^{-3}$ Ω cm for the A_3C_{60} metals, for a limiting conductivity $\sigma(0) = 800$ S/cm. This value comes from our measurements on crystalline thin films of K_3C_{60} and Rb_3C_{60}.[9,10] Slightly higher limiting conductivities have been obtained from other experiments.[8] We make use of the Fermi surface area obtained by Erwin[6] from LDA calculations, $S_F = 6.0 \times 10^{16}$ cm^2 (area of all of the sheets of the K_3C_{60} Fermi surface). [This value may be compared with the free electron estimates that may be obtained by the treatment given above: $S_F = 3.1 \times 10^{16}$ cm^2 (Case 1) and $S_F = 4.4 \times 10^{16}$ cm^2 (Case 2)]. Using the relationship $\sigma = (2\pi e^2/h)(12\pi^3)^{-1}(S_F l)$, we find $l = 2$ Å.

Mean Free Path (l) in κ-$ET_2Cu(NCS)_2$. . As may be seen from the log-linear plot given in Figure 3, we obtain a residual resistivity $\rho(0) = 1.0 \times 10^{-3}$ Ω cm for κ-$ET_2Cu(NCS)_2$, for a limiting conductivity $\sigma(0) = 1000$ S/cm. Extrapolation of the linear-linear plot given by Gartner, *et al.*,[18] gives a residual resistivity $\rho(0) = 0.4 \times 10^{-3}$ Ω cm, for a limiting conductivity $\sigma(0) = 2500$ S/cm. A measurement of the Fermi surface area in this salt is obtained from the Shubnikov-de Haas oscillations observed by Oshima, *et al.*[20]; they found that their experiments gave $S_F = 6.4 \times 10^{14}$ cm^2. However this value represents a lower limit to the area of all of the sheets of the Fermi surface; thus the correct area for use in the conductivity equation could be somewhat larger, as may be seen from the nature of the Fermi surface.[21] If we use the quoted value[20] in the relationship $\sigma = (2\pi e^2/h)(8\pi^3)^{-1}(S_F l)$, we find $l = 150 - 385$ Å (similar to previous estimates[22]).

Thus the mean free path calculated for κ-$ET_2Cu(NCS)_2$ is in accord with expectations for a metal (l > lattice constant), whereas the value found for the A_3C_{60} metals is anomalously short. This finding has been attributed to both merohedral disorder and strong electron-electron scattering.[6,8] Clearly the normal state conductivity of the A_3C_{60} metals deserves further attention.

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