Theoretical normal-state transport properties of K_3C_{60}

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Lowest-order variational solutions to Bloch-Boltzmann scattering theory are used in conjunction with first-principles band-structure results to predict the normal-state resistivity, Hall coefficient, and thermopower for K_3C_{60}. These properties, their pressure coefficients, and other Fermi-liquid-related parameters are compared with the available experimental data, with the goal of evaluating the extent to which these novel superconducting materials can be understood within the Fermi-liquid picture without strong correlations.

Since the initial demonstration of $T_c = 18$ K in K_3C_{60},[1] the superconducting properties of the A_3C_{60} compounds (A = alkali metal) have been the focus of intense scrutiny. Significantly less attention has been given to the normal-state properties of these metallic materials. Structural, spectroscopic, and transport measurements have been reported, but several fundamental questions remain to be addressed. Are these metals fundamentally bandlike materials, as assumed by several explanations of the superconductivity in terms of strong electron-phonon coupling,[2] or does the small intermolecular overlap lead to correlated carrier motion?[3] What effect does the observed orientational (merohedral) disorder of the A_3C_{60} phase[4] have on both normal and superconducting properties?

Regarding the first question, we note that calculations of the effective intramolecular Coulomb repulsion in a fulleride crystal lead to values of order 1 eV.[5] Since the calculated band width is 0.6 eV,[6] significant corrections to the band description may be necessary. Considering the three dimensionality, multiband character, and lack of strong Fermi-surface nesting, however, the band picture may well be more viable than the highly correlated limit. The effect of orientational disorder is also an open question: One study shows that *random* disorder rearranges the spectral density, although the electronic states remain itinerant.[7]

The experimental situation is not entirely clear either. Photoemission data[8] indicate an occupied band width for K_3C_{60} of ~ 1 eV, a factor of 4–5 larger than the calculated band width, possibly indicating strong electron correlation effects. However, Tycko *et al.*[9] have used the NMR spin-lattice relaxation rate (a bulk probe) to estimate a Fermi-level total density of states $N(\epsilon_F) \sim 35$ states/eV cell; the bulk and electron paramagnetic resonance magnetic susceptibility results are 31 and 22 states/eV cell, respectively.[10] These values are consistent with (if somewhat larger than) our calculated value of 13.2 states/eV cell, and are strongly suggestive of normal Fermi-liquid behavior.

One approach to these questions is to begin in a well-defined limit, calculate a number of normal-state properties, and then try to understand the corrections required in order to provide agreement with experiment. With this study, we begin such a program: Starting from the band viewpoint, we use first-principles electronic-structure results and formal expressions from Bloch-Boltzmann transport theory (assuming the normal state to be a standard Fermi liquid) to calculate several normal-state transport coefficients (resistivity, Hall coefficient, thermopower) and superconducting-state properties. Our results are summarized in Table I.

The validity of Bloch-Boltzmann theory rests on several conditions.[11] First is the nominal assumption that the carriers are quasiparticles in a periodic crystal, and hence have a well-defined dispersion relation ϵ_k. However, the formalism can be readily extended to impure crystals, and even to metallic alloys, where the excitations may not be quasiparticles at all, but for which the physical properties are qualitatively the same. Thus, the ob-

TABLE I. Calculated values of normal-state and superconductivity parameters for K_3C_{60}. Symbols are defined in the text.

Parameter	Value
Band width, W	0.61 eV
$N(\epsilon_F)$	13.2 states/eV cell (both spins)
v_F	1.77×10^7 cm/s
$\hbar\Omega_p$	1.22 eV
Λ (clean limit)	1600 Å
Λ (dirty limit)	3000–3500 Å
l (300 K)	7 Å/λ_{tr}
ρ (300 K)	$780\times\lambda_{tr}\,\mu\Omega$ cm
$\partial \ln\rho/\partial P$	-0.041 kbar^{-1}
R^H_{xyz}	0.70×10^{-8} m^3/C
$\partial \ln R^H_{xyz}/\partial P$	-0.003 kbar^{-1}
S (300 K)	-15.4 μV/k
$\partial S/\partial P$ (300 K)	~ 1 μV (K kbar)$^{-1}$

served merohedral disorder[4] in A_3C_{60} does not invalidate the *formalism,* but may only rearrange the spectral density and alter the quantitative predictions. Second, the scattering events are assumed to be independent, although phonons, defects, and even Coulomb scattering can be treated if their scattering rates are additive. We will concentrate on scattering by phonons. Although this scattering may be strong enough that the excitations (coupled electrons and phonons) are no longer quasiparticles, the formalism survives nevertheless. Finally, there is a question of how in general to describe an interacting electron-phonon system when the phonon frequencies approach the electron band width, which is the case in these materials.

We assume here a crystal with orientationally ordered C_{60} molecules. Rietveld refinements of powder x-ray data[4] have obtained good fits by assuming that two orientations are randomly populated. However, several workers have noted that even at very low temperatures, nominally "ordered" solid C_{60} actually contains substantial short-range disorder.[12,13] We suggest that A_xC_{60} materials that are "disordered" may (conversely) have some short-range order that could make our assumption of an ordered crystal more reasonable than it first appears.

For band metals with cubic symmetry, the resistivity is given by $\rho=4\pi/\Omega_p^2\tau$. The temperature dependence is contained in the scattering rate $1/\tau$, which is given[14] by variational solution of the scattering equation as

$$\hbar/\tau(T)=4\pi k_B T\int\frac{d\omega}{\omega}\alpha_{\rm tr}^2F(\omega)\left[\frac{h\omega/2k_BT}{\sinh(h\omega/2k_BT)}\right]^2 . \tag{1}$$

The integral is over all phonon frequencies and $\alpha_{\rm tr}^2F(\omega)$, the electron-phonon transport spectral function, is closely related to the spectral function $\alpha^2F(\omega)$ of Eliashberg theory. All of the band-structure effects are contained in the Drude plasma frequency, $\Omega_p^2=\frac{4\pi}{3}e^2v_F^2N(\epsilon_F)$, where v_F is the Fermi-surface-averaged electron velocity. For K_3C_{60}, we have used[6] local-density-approximation (LDA) band structure to calculate $v_F=1.8\times10^7$ cm/s, $N(\epsilon_F)=13.2$ states/eV, and the resulting Drude plasma frequency $\hbar\Omega_p=1.2$ eV. In BCS theory, this quantity determines the clean-limit London penetration depth, $\Lambda=c/\Omega_p=1600$ Å. The corresponding value for a dirty superconductor is larger by a factor $(1+\xi/l)^{1/2}$, where l is the mean free path and ξ is the intrinsic coherence length; this value is roughly 3000–3500 Å, in quite reasonable agreement with the reported values of 2400 Å (lower critical-field measurements[15]), 4800 Å (muon-spin relaxation[16]), and 6000 Å (NMR, Ref. 9).

We first examine the high-temperature behavior of the resistivity. At large T, the bracketed expression in Eq. (1) may be expanded to yield[17]

$$\hbar/\tau(T)\approx2\pi\lambda_{\rm tr}k_BT[1-O(\langle\omega^2\rangle_{\rm tr}/T^2)] , \tag{2}$$

where

$$\lambda_{\rm tr}=2\int(d\omega/\omega)\alpha_{\rm tr}^2F(\omega) .$$

From Eq. (2), it is clear that regardless of the shape of the transport spectral function, $\rho(T)$ will be linear in T at sufficiently high temperatures, with a slope proportional to $\lambda_{\rm tr}$. As its form suggests, $\lambda_{\rm tr}$ is closely related to the superconductivity coupling strength λ, and is within 10% of λ for a variety of metals.[18] For K_3C_{60}, theoretical estimates of λ range from ~0.5 to ~1.0. We will set $\lambda_{\rm tr}=1$, so that the resulting $\rho(T)$ may be considered either as semiquantitative or simply as normalized to this value.

For the A_3C_{60} compounds, $\langle\omega^2\rangle_{\rm tr}^{1/2}$ is of order 1000 K, making the linear approximation of Eq. (2) useless for temperatures of practical interest. Nevertheless, if there is sufficient spectral weight at low frequencies, this linearity will extend down to more modest temperatures as well. Suppose we take for the spectral function a single Einstein oscillator ω_0. Then for temperatures larger than $\omega_0/4$, the linear piece of Eq. (2) is within 20% of the exact solution. For a superposition of Einstein oscillators,

$$\alpha_{\rm tr}^2F(\omega)=\sum_i A_i\delta(\omega-\omega_i) , \tag{3}$$

contributions to $1/\tau(T)$ will be weighted by A_i/ω_i. Low frequencies are given extra weight in the integral, so that any nonlinearity in the resulting temperature dependence is limited to temperatures less than the lowest frequencies with appreciable spectral amplitude.

Although calculations[19] and experiments[20] by several groups have indicated which phonons may be important for electron pairing in K_3C_{60}, no detailed information exists for either $\alpha^2F(\omega)$ or $\alpha_{\rm tr}^2F(\omega)$. At the lowest level of approximation, $\alpha_{\rm tr}^2F(\omega)$ may be replaced by $F(\omega)$, the phonon density of states (DOS). Here we use results from inelastic neutron scattering[21] for the cross-section-weighted DOS, $G(\omega)$, in which the frequency range 20–1600 $\rm cm^{-1}$ was probed. By sampling $G(\omega)$ at 25 $\rm cm^{-1}$ intervals, we represent the spectral function in the form of Eq. (3), normalizing to $\lambda_{\rm tr}=1$. Carrying out the integration in Eq. (1) we obtain an explicit prediction for $\rho(T)$. The result, shown in Fig. 1, is indeed remarkably linear down to 50 K, a consequence of substantial low-frequency intensity in $G(\omega)$. From numerical solution of the Eliashberg equations, Dolgov and Mazin[19] have concluded that there must be a very low-frequency peak in α^2F, and presumably in $\alpha_{\rm tr}^2F$ as well. Any such additional weight would make $\rho(T)$ even more linear. Here, we note a slight ($\sim20\%$) supralinear effect over the range

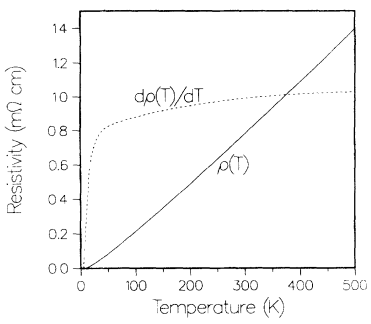

FIG. 1. Calculated normal-state resistivity, $\rho(T)$, and $d\rho(T)/dT$ (arbitrary units) for K_3C_{60}.

50–500 K. The room-temperature resistivity is calculated to be $\sim 800\lambda_{tr}$ $\mu\Omega$ cm. We also calculate the intrinsic room-temperature mean free path to be $l=7$ Å$/\lambda_{tr}$, at the Ioffe-Regel limit (the lower limit of validity for Bloch-Boltzmann theory). The theory will be valid at lower temperatures.

To extract the pressure dependence of $\rho(T)$, we recalculate the self-consistent LDA band structure at a lattice constant 0.2 Å larger than equilibrium. The bands are quite sensitive to small changes in lattice constant: In this case, the relevant band width is decreased by 21%. The dependence of τ on lattice constant is not simply determined, so we assume to first order that $1/\tau \sim \lambda_{tr} \sim \lambda \sim N(\epsilon_F)$. Using the measured compressibility of K_3C_{60},[22] we calculate the pressure derivative of the relative change in resistivity to be $\partial \ln\rho/\partial P = -0.041$ kbar^{-1}.

Several measurements of the resistivity have been reported. Maruyama *et al.*[23] have found $\rho(T_c)=8$ mΩ cm and a slope of ~ 15 $\mu\Omega$ cm/K. Rotter *et al.*[24] have reported a much smaller value of $\rho(T_c)=0.4$ mΩ cm, inferred from reflectivity measurements, which is a less direct result but is also less prone to granularity effects. Recent single-crystal measurements by Xiang *et al.*[25] find $\rho(T_c)=2.5$ mΩ cm and $\rho(280\text{ K}) = 5$ mΩ cm. This variation in measured values indicates that the intrinsic bulk resistivity has probably not yet been achieved, but the best resistivities are beginning to approach our calculated value (if $\lambda_{tr}\sim 1$).

The Hall coefficient is given by a ratio of transport coefficients, $R^H_{xyz}=E_y/j_xB_z=\sigma_{xyz}/\sigma^2$, where $\sigma=1/\rho$ is the conductivity, and the Hall conductivity is given explicitly by

$$\sigma_{xyz}=-\left[\frac{e^3\tau^2}{8\pi^3\hbar}\right]\int_{BZ} d^3k\, v_x(\mathbf{k})[\mathbf{v}(\mathbf{k})\times\nabla_{\mathbf{k}}v_y(\mathbf{k})]_z\left[-\frac{\partial f}{\partial\epsilon_{\mathbf{k}}}\right]. \tag{4}$$

The overall sign is a weighted average of the curvature of the Fermi surface; for a free-electron gas, the result $R^H=-1/ne$ is recovered. Since the result for a hole sphere has the opposite sign, the sign of the Hall coefficient is frequently interpreted as giving the carrier type. We caution that the K_3C_{60} Fermi surface is quite complex,[6] with regions of both positive and negative curvature, so that the interpretation of R^H_{xyz} in terms of a carrier type and density becomes somewhat meaningless. For isotropic scattering (i.e., the high-T regime), R^H_{xyz} is temperature independent. At temperatures for which only low-Q phonons are available to scatter electrons across the Fermi surface, anisotropy in the Fermi surface may be manifested as a strong temperature dependence; we do not treat this effect here.

In Fig. 2 we show, for pedagogical purposes, the energy dependence of R^H_{xyz} within a rigid-band assumption for band fillings from 0 to 6 electrons (note that actual A_xC_{60} materials are *not* rigid-band systems). Near the bottom and top of the band, R^H_{xyz} is accurately given by the free-electron and free-hole expression, respectively. The Hall coefficient at the K_3C_{60} Fermi level is positive ("hole-like") and has the value $R^H=+0.70\times10^{-8}$ m^3/C. Because of the nearby sign change, which results from large cancellation of curvatures, the precise value may be sensitive to small details of the bands, thus disorder may strongly affect R^H. The spike at 0.1 eV coincides with a strong dip in the electronic density of states, separating the two lower bands from the upper one; the dip is manifested here as a multiband effect.

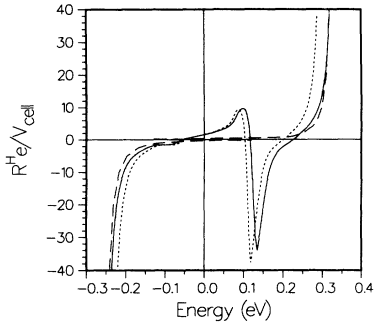

FIG. 2. Energy dependence of the calculated Hall coefficient R^H (solid curve). The Fermi level, and the predicted value for R^H, is at the energy zero; values for other energies assume a rigid-band behavior. The lower and upper dashed curves are the free-electron and hole Hall coefficients, respectively. The dotted curve refers to the expanded lattice (see text). The dimensionless quantity (*e*/cell-volume)$R^H=1/N$ is plotted, where N is the (signed) effective number of carriers per cell.

Figure 2 also shows the energy dependence of R^H_{xyz} for the expanded lattice. The primary effect of the expansion is to compress the bands, more or less about the midpoint (which is very close to the Fermi level). On the scale of the plot, R^H_{xyz} at ϵ_F is unchanged, reflecting only subtle changes in the Fermi-surface curvature. Indeed, the calculated relative pressure derivative is quite small, $\partial \ln R^H_{xyz}/\partial P = -0.003$ kbar^{-1}.

We are only aware of a single Hall measurement, for K_3C_{60} thin films.[26] At low temperatures, a Hall coefficient of roughly -0.3×10^{-9} m^3/C was obtained. The observed strong temperature dependence makes comparison to our T-independent value problematic, and in any event, sample granularity makes the thin-film data very difficult to relate to bulk values.

The lowest-order variational solution for the thermopower is

$$S=-\left[\frac{e}{8\pi^3\sigma T}\right]\int_{BZ} d\epsilon\, N(\epsilon)v_x^2(\epsilon)\tau(\epsilon)(\epsilon-\epsilon_F)\left[-\frac{\partial f}{\partial\epsilon_{\mathbf{k}}}\right]. \tag{5}$$

We allow for an energy dependence in τ, so that (for T not too small) we have

$$\hbar/\tau(T,\epsilon)\approx 2\pi\lambda_{tr}(\epsilon)k_BT\ .$$

We have treated this energy dependence at two levels of approximation: (1) $\lambda(\epsilon)=$constant, and (2) $\lambda(\epsilon)\propto N(\epsilon)$, while including the full energy dependence of the band

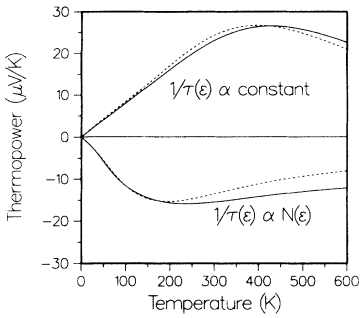

FIG. 3. Temperature dependence of the thermopower, $S(T)$, using two different assumptions for the energy dependence of the scattering rate. The dotted curves are for the expanded lattice.

properties. The resulting $S(T)$ are shown in Fig. 3. At moderate temperatures, the first approximation leads to a free-hole-like thermopower (linear in T with positive slope). The second approximation gives quite different results, showing electronlike behavior up to ~ 200 K and a slow transition to positive slope thereafter. The qualitatively different high-T behavior arises from sensitivity to variations in $N(\epsilon)$ within a few kT of the Fermi level.

Figure 3 also shows thermopower curves for the expanded lattice; the pressure dependence of $S(T)$ apparently depends on both $\lambda(\epsilon)$ and T in a complicated fashion. For $\lambda(\epsilon) \propto N(\epsilon)$, there is a rough division into two temperature regimes: For $T < 250$ K, the pressure derivative of $S(T)$ is very small or zero, while for $T > 250$ K, it rises to a roughly T-independent value of $\partial S/\partial P \sim 1$ μV (K kbar)$^{-1}$.

Measurements of the thermopower show negative linear behavior up to 300 K, with room-temperature values in the range 10–20 μV/K.[27,28] The absence of substantial deviation from linearity may be an indication that $N(\epsilon)$ has less structure than we calculate, either due to merohedral disorder or to crystal defects.

At this stage, no definitive conclusions can be drawn regarding the validity of the Fermi-liquid-based Bloch-Boltzmann picture for K_3C_{60}. Resistivity measurements on improved samples give results in qualitative agreement with Bloch-Boltzmann theory, but uncertainties about the coupling strength and sample quality preclude definite conclusions. Thermopower measurements are consistent with calculated values, but again it is premature to draw specific conclusions. Further transport data on well-characterized single crystals are needed. We have provided a compendium of physical parameters against which to compare future experimental results.

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