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Orientational disorder and normal-state electronic-transport properties of A_3C_{60}

Martin P. Gelfand and Jian Ping Lu*

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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A model proposed for the conduction band of alkali-metal-doped C_{60}, which allows for experimentally relevant orientational disorder, is further analyzed. Transport properties are calculated by evaluation of Kubo-Greenwood formulas on finite systems. The residual resistivity is close to 400 $\mu\Omega$ cm; the thermal conductivity satisfies the Weidemann-Franz law; and the thermopower varies as the inverse of the conduction bandwidth with a known coefficient, making possible quantitative estimates of the density of states. The comparison with experimental results appears favorable.

In a recent paper[1] we suggested that intrinsic orientational disorder in the alkali-metal-doped fullerides A_3C_{60} (Ref. 2) might have a substantial influence on the electronic properties of these materials. By constructing a tight-binding model for the molecular t_{1u} orbitals comprising the conduction band and calculating the states for supercells of up to 6^3 standard fcc unit cells, we demonstrated that the density of states changes dramatically on going from the (experimentally inaccessible, but theoretically convenient) ordered $Fm\bar{3}$ structure to a maximally disordered $Fm\bar{3}m$ structure. Although only states close to the band edges were found to be localized in the latter case, we argued that the transport mean free path at the band center should nonetheless be short, of order the inter-C_{60} spacing, because the disorder in the hopping amplitudes is not small and is uniformly present at that length scale. However, we presented no calculations in support of that claim. The present work describes such calculations. Specifically, we evaluate Kubo-Greenwood formulas on finite systems to estimate the electrical conductivity and the (electronic contribution to the) thermal conductivity and thermopower.

We first summarize the principal results of the calculations, and later describe the method of calculation, give further details of the results, and speculate on the reliability of our approach to the problem of normal-state properties of metallic A_3C_{60} compounds.

For Rb_3C_{60} or K_3C_{60}, we estimate the *residual resistivity* to be 390 $\mu\Omega$ cm, with a statistical uncertainty of $\pm 5\%$. (To be more precise, K_3C_{60} might have a residual resistivity roughly 1–2 % smaller than Rb_3C_{60} due to its smaller lattice constant, but the difference is, for now, experimentally irrelevant.) This result is in good agreement with the somewhat indirect estimate of the dc residual resistivity of Rb_3C_{60} obtained by the far-infrared reflectivity study of Rotter *et al.*,[3] namely, 400 $\mu\Omega$ cm. It is also consistent with the suggestion of Palstra *et al.*[4] and Kochanski *et al.*[5] that the minimum resistivity of thin films, somewhat greater than 2000 $\mu\Omega$ cm for K_3C_{60}, is not intrinsic but, rather, dominated by effects of granularity. Two further remarks follow: (1) this estimate of the residual resistivity is independent of the overall scale of the hopping amplitudes and is thus unaffected by the fact that ours may be much too small,[1] and (2) by inspection of $\sigma(\omega)$ one finds that the transport mean free time τ_{tr} is of order $\hbar/W$, with W the conduction bandwidth, so crystal momentum is not conserved on any meaningful time scale.

The electronic contribution to the *thermal conductivity* κ appears to satisfy, within statistical errors, the Weidemann-Franz law $\sigma/\kappa T = (\pi^2/3)(e^2/k_B^2)$ at low temperatures. Since we are only considering the effects of elastic scattering on the conduction electrons this result is not too surprising. Indeed, the Weidemann-Franz law is thought to hold for the electronic part of κ in amorphous metals.[6]

Finally, the *thermoelectric power* S has been calculated; the results are contrary to our initial expectations and are thus particularly interesting. We had anticipated[1] that the thermopower would be p-type, because $dN/dE < 0$ at the Fermi energy. Instead, the calculations yield an n-type thermopower, which is consistent with recent experimental data.[7] Comparison of the magnitudes of the experimental and calculated values of S enables one to estimate the conduction bandwidth W. We thus find for K_3C_{60} $W \approx 240$ meV and a density of states at the Fermi level $N(\epsilon_F)$ of about 13 states/eV per spin per C_{60} [and for Rb_3C_{60}, half that W and twice that $N(\epsilon_F)$], but the numerical results for the thermopower are not as clear-cut as for the electrical and thermal conductivity and the uncertainty accompanying these estimates is large. (Note that the measured thermopower can be close to its intrinsic, metallic value even in samples for which the electrical resistivity is dominated by intergrain contacts;[8] hence the comparison with the experimental results of Inabe *et al.*[7] may be meaningful.) Modern electronic-structure calculations[9] for K_3C_{60} in the $Fm\bar{3}$ structure typically yield similar values for $N(\epsilon_F)$, but values for W twice as large. [Such calculations often find ϵ_F near a sharp peak in $N(\epsilon)$, so it is better to look at the bandwidths.] Present experimental estimates of $N(\epsilon_F)$ by methods such as nuclear and electron spin resonance[10] are still unsettled, but typically in the range 10–20 states/eV per spin per C_{60} for K_3C_{60} with somewhat large values found for Rb_3C_{60}. Our estimate of $N(\epsilon_F)$ is based on entirely different assumptions than

those applied in the interpretation of resonance data, and thus we find encouraging the degree to which these very different probes yield consistent results.

The tight-binding model underlying our results may be expressed in the form

$$H = \sum_{\langle i,j\rangle\alpha\beta\sigma} t^{(R)}_{i\alpha,j\beta}(c^{\dagger}_{i\alpha\sigma}c_{j\beta\sigma} + \text{H.c.}), \tag{1}$$

where $\langle i,j\rangle$ label (nearest-neighbor) sites on a fcc lattice, α,β label molecular orbitals (specifically, the t_{1u} orbitals from which the conduction band is derived), σ is the spin index, and R describes the orientations of the molecules. For a given (suitably random[1]) configuration the hopping amplitudes $t^{(R)}_{i\alpha,j\beta}$ were calculated by the primitive method described in Ref. 1.[11] Most calculations discussed in this paper are for the case of "maximum orientational disorder" as defined in Ref. 1. Presumably one could do a better job of calculating the hopping amplitudes (see, for example, Gunnarsson *et al.*[12] and Menon and Subbaswamy[13]) but we thought it worthwhile to fully explore the consequences of the model we had at hand. Others might well want to perform analogous calculations using their preferred set of hopping amplitudes; the comparison with ours could be useful.

The calculations of transport properties are direct implementations of Kubo-Greenwood[14] formulas, which for noninteracting electrons relate transport properties to matrix elements between exact single-particle states. For the electrical conductivity, the formula may be written as

$$\sigma(\omega) = \tfrac{2}{3}\pi e^2 \sum_{m,m'} (N_c a^3\omega)^{-1}[f(\epsilon_{m'}) - f(\epsilon_m)] \times\delta(\epsilon_{m'} - \epsilon_m - \hbar\omega) \times\langle m'|\mathbf{J}|m\rangle\cdot\langle m|\mathbf{J}|m'\rangle, \tag{2}$$

where a is the fcc lattice constant, N_c is the number of standard cells (and hence $N_c a^3$ is the volume), m,m' label exact single-particle states, ϵ_m's are energy eigenvalues, f is the Fermi distribution, and $\mathbf{J}$ is the particle current. Because the tight-binding model contains no spin-flip processes, we take the kets $|m\rangle$ to describe strictly the spatial and molecular orbital degrees of freedom, with the only effect of spin being the factor of 2 in Eq. (2). Henceforth we consider the conductivity only at $T = 0$. Since the $\mathbf{J}$ contains a factor of $a/2\hbar$ one can rewrite Eq. (2) in the form

$$\sigma(\omega) = (\pi e^2/6\hbar a)\bar{\sigma}(\omega), \tag{3}$$

where $\bar{\sigma}$ has no explicit dependence on the lattice constant.

There are a few other obvious properties of $\bar{\sigma}(\omega)$ worth pointing out: It is dimensionless, it should become independent of system size for large enough systems (in practice, 4^3 fcc cells was sufficient at maximal orientational disorder), and if all hopping amplitudes t are multiplied by the same factor ξ then the old and new $\bar{\sigma}$ are related simply by

$$\bar{\sigma}_t(\omega) = \bar{\sigma}_{\xi t}(\xi\omega). \tag{4}$$

This last property implies that the calculated dc conductivity is independent of the overall scale of the hopping amplitudes. Thus, the fact that our primitive calculation of the hopping amplitudes yields values which may be far too small is irrelevant; what counts is that they are probably in the correct proportions.[1,11] From the viewpoint of Boltzmann transport theory, one would say that rescaling t alters both the relaxation time and the Fermi velocity in such a way that their effects cancel.

In order to apply Kubo-Greenwood formulas for finite systems, it is necessary to "smear" the δ functions at the discrete transition energies over some energy scale η, where η must be large compared to the spacing between transitions but small compared to any physically relevant scale, such as $\hbar/\tau_{\text{tr}}$. We checked that the results were independent both of η within the appropriate range and also of the choice of smearing function.

For Rb_3C_{60}, in which $a = 14.4$ Å, one may rewrite Eq. (3) as $\rho_{\text{dc}} = (1130\ \mu\Omega\,\text{cm})/\bar{\sigma}(0)$. Figure 1 shows $\bar{\sigma}(\omega)$ for the case of maximal orientational disorder and a half-filled conduction band; an estimate of $\bar{\sigma}(0)$ obtained by crude extrapolation is indicated on the vertical axis, namely, 2.90 ± 0.15. The resulting estimate of ρ_{dc} is, as stated above, 390 ($\pm5\%$) $\mu\Omega\,\text{cm}$. We have not yet explored in detail the consequences of reducing the disorder. It seems that the elastic mean free path grows fairly quickly with reduced disorder in addition to the development of new structure in $\sigma(\omega)$ suggestive of a narrow Drude peak; however, calculations on larger systems are required to reach definite conclusions.

Now let us turn to the thermal conductivity. The Kubo-Greenwood formula for the electrical conductivity (2) may be expressed in shorthand as $\sigma = e^2 L_{nn}$ where n denotes particle current.[16] If we let a subscript q denote heat current (see Mahan[17] for a definition of the heat current in tight-binding models), then the analogous formula for thermal conductivity is

$$\kappa = (1/T)[L_{qq} - L^2_{nq}/L_{nn}], \tag{5}$$

where the L_{qq} has the same form as L_{nn} except that the particle current operators are replaced by heat current operators $\mathbf{J}_q$; likewise for L_{nq}. In our calculations the

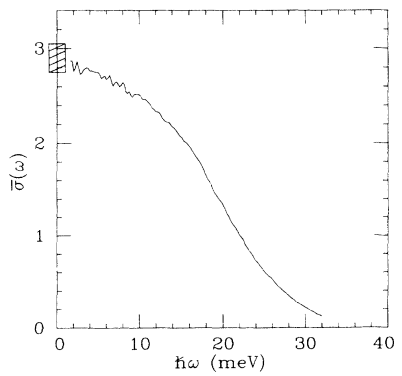

FIG. 1. Plot of $\bar{\sigma}(\omega)$ vs $\hbar\omega$ for a single $N_c = 5^26$, maximally disordered system. The estimated value of $\bar{\sigma}(0)$, with conservative error bars, is indicated on the vertical axis. Note that the conduction bandwidth for our model is close to 40 meV, and that the shape of the curve is far from Lorentzian.

second term in the brackets is neglected, since both L_{qq} and L_{nq} are expected to vary as T^2 at low temperature.[15] We also neglect the variation of chemical potential with temperature; however, dN/dE is quite small at the Fermi energy,[1] so this should not be a significant source of error, either.

As in the case of the electrical conductivity, it is not hard to see that at low enough temperature the electronic contribution to the thermal conductivity is invariant under a uniform rescaling of the hopping matrix elements. By simple manipulations one may cast the Kubo-Greenwood formula in the form

$$\kappa(\omega,T) = (\pi/6T\hbar a)\bar{\kappa}(\omega,T), \tag{6}$$

where $\bar{\kappa}$ depends only on ω, T, and the hopping amplitudes; under rescaling of the latter one finds

$$\xi^2\bar{\kappa}_t(\omega,T) = \bar{\kappa}_{\xi t}(\xi\omega,\xi T). \tag{7}$$

Then in the zero-frequency limit, assuming that the thermal conductivity is linear in temperature, one has $\kappa_t(T) = \kappa_{\xi t}(T)$.

Let us now discuss the numerical results. In Fig. 2, $\bar{\kappa}$ for an $N_c = 4^3$, maximally disordered system is plotted for eight values of T ranging from about 0.5% to 6% of the bandwidth. By extrapolating these data to $\omega = 0$ we estimate $\bar{\kappa}/T^2 = 9.33 \pm 5\%$ so that the dimensionless version of the Lorenz number, $e^2\kappa/k_B^2\sigma T \equiv \bar{\kappa}/T^2\bar{\sigma}$, equals $3.22 \pm 7\%$; as expected, this is consistent with the Weidemann-Franz value $\pi^2/3 = 3.29$.

In terms of the L functions described above, the thermopower is given by

$$S = -(1/eT)(L_{nq}/L_{nn}), \tag{8}$$

where e is the *magnitude* of the electron charge. The temperature dependence of L_{nn} (i.e., of the electrical conductivity) will be neglected below since the temperature dependence of L_{nq} is much stronger. We define $\bar{S}$ via

$$L_{nq} = (\pi/6\hbar a)\bar{S}\ , \tag{9}$$

so that $S = -(1/eT)(\bar{S}/\bar{\sigma})$, and carry out numerical calculations for $\bar{S}$, which depends only on ω, T, and the hopping amplitudes. Upon rescaling of the hopping amplitudes, one sees that

$$\xi\bar{S}_t(\omega,T) = \bar{S}_{\xi t}(\xi\omega,\xi T) \tag{10}$$

so in the $\omega \to 0$ limit, and assuming $\bar{S} \sim T^2$, the thermopower varies with the rescaling parameter as ξ^{-1}. This result is consistent with the expression for the thermopower from Boltzmann transport theory,[15] $S \propto \partial \ln\sigma/\partial\epsilon_F$, in which the scaling of S with the inverse of the bandwidth is apparent. To the extent that the tight-binding model is correct up to an overall scale factor, comparison of the present calculations with experimental values for the thermopower can provide a direct measure of the bandwidth.

Unfortunately, numerical results for $\bar{S}$ are not as readily obtained as in the cases of $\bar{\sigma}$ and $\bar{\kappa}$. Unlike the latter, the Kubo-Greenwood formula for S yields a sum of δ functions with both positive and negative amplitudes. At low temperature $S \to 0$, one is in the position of estimating a small quantity as a difference of large quantities; naturally the fluctuations can be large compared to the average. In order to have any confidence in the results from a single sample, it is necessary to perform calculations for systems of at least 5^3 fcc cells; in contrast, for the conductivity 3^3 can suffice. Furthermore, there are substantial sample-to-sample fluctuations even for systems that large.

We have calculated $\bar{S}(\omega)$ for four maximally disordered systems with $N_c = 5^3$ and averaged over this small ensemble; the data are not displayed due to space constraints. We extrapolated to $\omega = 0$ using simple averaging as well as linear fits over various frequency ranges. The resulting estimates for $S(T)$, for T ranging from 1.3% to 10% of the bandwidth, are plotted as error bars on Fig. 3. There are two conclusions one might draw from this figure: Either $S(T)$ really is nonlinear at very low temperature, so there is an energy scale much less than the bandwidth which was not evident in the temperature dependence of κ or the frequency dependence of σ; or this result is due to the large sample-to-sample fluctuations. Both are tenable: An obvious feature of the $N_c = 5^3$ data is that dS/dT for the "high"-T ($T \gtrsim 20$ K) data is roughly the same for every sample, even though the in-

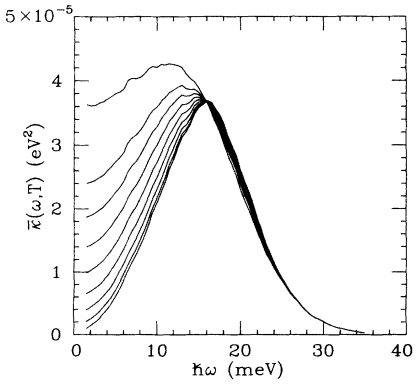

FIG. 2. Plots of $\bar{\kappa}(\omega,T)$ vs $\hbar\omega$ for a single $N_c = 4^3$, maximally disordered system at temperatures $k_BT = 0.2$, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, and 2.0 meV (from bottom to top, at small frequencies).

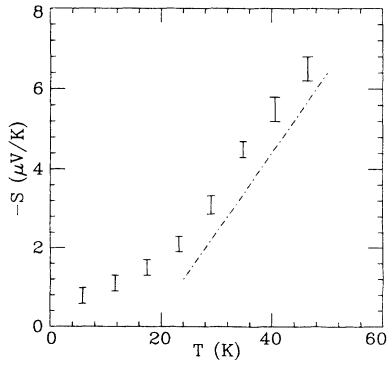

FIG. 3. Plot of estimated S vs T, obtained by averaging over four systems of size $N_c = 5^3$. The dotted-dashed line has slope 0.2 μV/K^2.

tercepts on the S axis vary widely; on the other hand, the nonlinearity persists even after averaging over 85 samples of size $N_c = 4^3$. What is most relevant for comparison with the experiments, however, is dS/dT at "high"-T, which for our model is approximately -0.2 μV/K^2 in both the $N_c = 5^3$ and 4^3 numerical data.

Experiments[7] on K_3C_{60} and Rb_3C_{60} yield $dS/dT \approx -0.033$ and -0.066 μV/K^2, respectively. These results indicate that our model's bandwidth of 40 meV requires rescaling by factors of 6 and 3, to roughly 240 and 120 meV, respectively. The experiments show $S(T)$ to be almost perfectly linear from 150 to 300 K (which is the part of the data we use to estimate dS/dT), with noticeable deviations from linearity at lower temperatures. However, until the experimental results are reproduced independently one should view our estimates of W and $N(\epsilon_F)$ as preliminary.

Let us now summarize and assess the work presented here. Starting from a specific model of static orientational disorder in A_3C_{60} we have calculated the normal-state transport properties associated with electrons in the conduction band. The calculated conductivity is consistent with the only experimental estimate to date of the intragranular conductivity.[3] The calculated thermopower, when compared with experimental results,[7] provides an estimate of the conduction bandwidth and $N(\epsilon_F)$ which seems plausible; this method of determining $N(\epsilon_F)$ complements well other probes such as NMR. What is perhaps most striking is that the agreement with experiment is apparently good even though electron-phonon couplings have been completely ignored in the calculations. Proposals for superconductivity based on strong coupling to phonons should be critically examined in this light.

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*Present address: Department of Physics and Astronomy, The University of North Carolina at Chapel Hill, CB#3225, Phillips Hall at Chapel Hill, NC 27599-3255.

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[11] In the calculations presented below we use the matrix elements derived for a lattice spacing $a = 14.2$ Å, relevant to K_3C_{60}. However, we have checked that upon increasing a to 14.4 Å ratios of the various matrix elements are nearly unchanged even as their overall scale decreases by 33%, and, furthermore, our conduction-band dispersion for the ordered structure agrees well with local-density-approximation calculations; hence we believe the results are correct modulo the effects of overall rescalings of the matrix elements. These effects are discussed in detail in the text.

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[16] The "L" notation basically follows that of Mahan (Ref. 17), except that (1) our L's lack an explicit factor of T compared with those in Ref. 17, (2) the expressions for the L's are generalized (albeit formally, for L_{nq} and L_{qq}) to nonzero frequency and specialized to the case of noninteracting electrons.

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