Orientational Disorder and Electronic States in C_{60} and A_3C_{60}, where A is an Alkali Metal

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Orientational disorder appears to persist in solid C_{60} even at low temperature, and similar static disorder is likely to exist in A_3C_{60}. The effects of such disorder on their electronic structures are studied by three-band tight-binding models for the C_{60} and A_3C_{60} conduction bands. The densities of states for the disordered systems are quite different from those in the ordered systems. Participation-ratio analyses suggest that most of the states are delocalized, but there should nonetheless be a host of experimental consequences associated with short mean free paths.

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Solid C_{60} in its most common form and the alkali-metal-doped phases A_3C_{60} have similar crystal structures: The C_{60} molecules sit on fcc lattice sites and the dopant ions (when present) occupy the tetrahedral and octahedral interstices. This description does not fully characterize the structures: Because C_{60} is not perfectly spherical the question of its orientation arises. For pure C_{60}, a first-order transition at 260 K from free rotation to a $Pa\bar{3}$ structure has been seen in x-ray [1] and neutron scattering measurements [2]. Both theoretical investigations [3] and experiments [2] suggest that below 260 K there remains a substantial amount of disorder associated primarily with two inequivalent orientations (related by $\pi/3$ rotation about a threefold axis) which are separated by potential barriers of roughly 300 meV. At lower temperatures, 90–160 K depending on the frequency of the probe, the hindered rotation appears to freeze out [2,4]. David *et al.* [2] estimate that at low temperatures the two low-energy orientations are found in a 5:1 ratio.

In K_3C_{60}, the structure at room temperature is believed to have the space group $Fm\bar{3}m$ [5]: Two inequivalent orientations, related by $\pi/2$ rotation about a twofold axis, have equal probability. Orientational transitions analogous to those in pure C_{60} have not yet been clearly elucidated. Recent ^{13}C NMR measurements [6] suggest that at room temperature molecular reorientation is frequent in K_3C_{60} but already substantially hindered in Rb_3C_{60}. In both compounds the barriers to rotation are likely to be higher than those in the undoped material, so when the molecular orientations do freeze there should be more disorder than in undoped C_{60}.

Given that orientational disorder may be unavoidable in both pure and doped C_{60}, what are its consequences for electronic properties? There have been several studies of the electronic structure of C_{60} and A_3C_{60} using state-of-the-art methods [7–10]. These studies find significant structure in the conduction-band density of states, and, for K_3C_{60}, a rather complex Fermi surface [8]. For practical reasons, these calculations assumed complete orientational order. (Some calculations for pure C_{60} have used a crystal structure which is now known not to be appropriate; fortunately, it is exactly the $Fm\bar{3}$ structure that corresponds to fully aligned molecules in A_3C_{60}, so we can compare it with other calculations for A_3C_{60}.) The conduction band is formed by hybridization of the triply degenerate molecular t_{1u} orbitals; these are rather like atomic p orbitals. Mott and Davis [11] have argued that, quite generally, bands derived from non-spherically-symmetric orbitals should be very different in the crystalline and amorphous forms of a solid, and disorder cannot be viewed as a small perturbation. We have investigated the conduction-band states of C_{60} and A_3C_{60} in the presence of the specific types of static orientational disorder one expects to find at low temperatures, as described above, to see whether Mott and Davis' suggestion might apply in these cases. Although our calculations might well be characterized as primitive (not *ab initio*, nor even self-consistent field), we believe they are adequate to demonstrate that the effects of disorder are indeed significant.

The tight-binding models we derive make no reference to any dopants, and treat them simply as sources of electrons for the C_{60} conduction band; only the positions and orientations of the C_{60} molecules are significant. The molecular centers were taken to lie on a perfect fcc lattice, with lattice constant 14.2 Å for the A_3C_{60} structure (corresponding to $A=K$) and 14.04 Å for the pure C_{60} structure. For more detailed descriptions of the low-energy molecular orientations we refer the reader to Refs. [2,3,5].

The first step in the calculation is to treat each C_{60} molecule as a sixty-site, one-band nearest-neighbor tight-binding model, with the sites corresponding to radially directed carbon p_π orbitals. Such an approach ("Hückel theory") yields molecular orbitals near the Fermi level which are in excellent agreement with more sophisticated calculations. The ratio of hopping amplitudes for the short (≈ 1.40 Å) and long (≈ 1.45 Å) C-C bonds was taken as 1.2 for the calculations presented here. This value is in the range suggested by Elser and Haddon [12]; taking instead the value 1.0 changes the results insignificantly.

Following diagonalization of the molecular tight-binding model, the intermolecular resonance integrals (also known as hopping amplitudes) for the t_{1u} orbitals were calculated by closely following LeBlanc's treatment of solid anthracene [13]. The hopping amplitudes for the cases of "parallel" and "perpendicular" (rotationally equivalent or inequivalent) neighbors in the A_3C_{60} structure are given in Table I. They are noticeably different, despite the fact that the four nearest-neighbor C-C distances change (decrease) by only about 1% on going from the parallel to perpendicular configuration; the difference is due primarily to changes in the phases of the relevant molecular wave functions.

The hopping amplitudes calculated here are only a few meV, so the resulting bandwidths are much smaller than those found by more sophisticated methods. However, the resulting conduction-band dispersions for the fully ordered systems (all molecules parallel in A_3C_{60}, all identically rotated about the appropriate 111 axes in the $Pa\bar{3}$ structure for pure C_{60}) are quite similar to the results of the self-consistent local-density-approximation calculations except for the magnitudes of the bandwidths (a factor of 10 for A_3C_{60}, a factor of 15 for C_{60}). For the $Fm\bar{3}$ structure relevant to A_3C_{60}, compare Fig. 1 with Fig. 4(b) of Saito and Oshiyama [7,14]. For the $Pa\bar{3}$ structure relevant to pure C_{60}, compare Fig. 2 with Fig. 11 of Satpathy *et al.* [10]. (These figures also show our calculations of the valence bands. For the $Pa\bar{3}$ crystal structure, a new result is that the band gap is apparently indirect, from Γ to *R*. We will not discuss the valence bands further in this paper.) These results are not surprising, given the history of band-structure calculations for anthracene as described by Silinsh [15]. LeBlanc's calculation gave a bandwidth which was about a factor of 10 smaller than later calculations, but the anisotropy in the conduction band was in reasonable agreement with experiment and later, more sophisticated calculations. Thus we concede that the magnitudes of the hopping amplitudes are seriously underestimated by our calculations, but, as the symmetries of the orbitals and the bands for the ordered systems are well described, we believe that the orientational dependence should also be adequately described. The energy units are therefore omitted in the plots that follow.

TABLE I. Hopping amplitudes in the A_3C_{60} structure, in units of meV, for molecules with center-to-center vector 110 (for different vectors, the elements of the matrices are permuted and/or change sign). The t_{1u} orbitals were chosen so as to transform as x,y,z under elements of the icosahedral group. "Parallel" and "perpendicular" indicate orientationally equivalent and inequivalent molecules, respectively. (Note that x,y,z refer to local coordinate systems which differ by $\pi/2$ rotation about z for orientationally inequivalent molecules.)

	Parallel			Perpendicular		
	x	*y*	*z*	*x*	*y*	*z*
x	0.83	−1.98	0.00	1.75	2.08	0.00
y	−1.98	3.36	0.00	−2.08	−3.71	0.00
z	0.00	0.00	−1.91	0.00	0.00	−2.67

The densities of states $N(E)$ for the fully ordered systems (see Figs. 3 and 4) have substantial structure: deep minima, sharp peaks, and for A_3C_{60} a tail down to the minimum energy at the *X* point. For disordered systems, we calculated eigenvalues and eigenstates for up to 6^3 cubic cells (864 molecules) with periodic boundary conditions, and averaged over ensembles for various amounts of uncorrelated orientational disorder. For maximum disorder, i.e., equal probability for the two possible orientations at each site, the densities of states are also shown in Figs. 3 and 4. For A_3C_{60} the peaks and valleys of the ordered structure are completely washed out, and the low-energy tail is gone. Instead, the density of states is a rather smooth function. Remarkably, the density of states at the Fermi level (for three electrons per molecule) differs by only a few percent from that in the or-

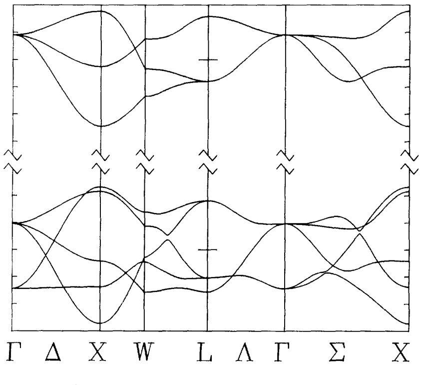

FIG. 1. Conduction- and valence-band dispersions for the $Fm\bar{3}$ structure. The marks at the *L* point indicate the energies of the molecular orbitals from which the bands are derived; the spacing between tick marks on the vertical axes corresponds to 10 meV.

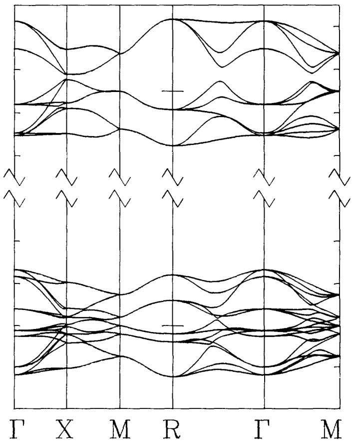

FIG. 2. Conduction- and valence-band dispersions for the $Pa\bar{3}$ structure (otherwise, same as Fig. 1).

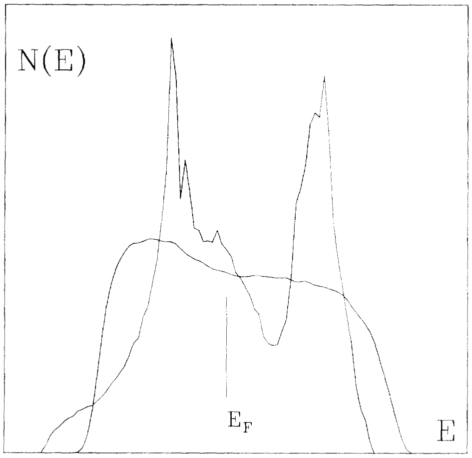

FIG. 3. Densities of states vs energy for the $Fm\bar{3}$ structure and its maximally disordered version; the former is the one with two large peaks. The Fermi energy for three electrons per molecule is indicated; it is nearly unchanged upon disordering.

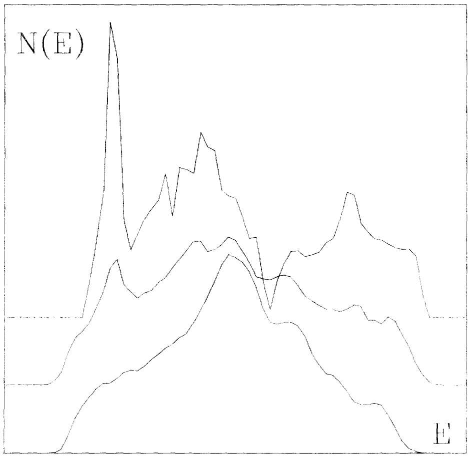

FIG. 4. Densities of states vs energy for the $Pa\bar{3}$ structure (top), a disordered version with a 4:1 occupation ratio for the two inequivalent orientations (middle), and the maximally disordered version (bottom). The plots were displaced vertically for clarity.

dered system. For C_{60} the disorder produces a new structure, a broad peak near the center of the band, while eliminating all the features of the pristine density of states. Upon reducing the degree of disorder the densities of states evolve smoothly towards their values in the ordered systems (see Fig. 4).

Are the changes in the densities of states produced by maximum disorder accompanied by localization of a large fraction of the states? Calculations of the participation ratio as a function of energy for the maximally disordered A_3C_{60} structure, shown in Fig. 5, suggest that the answer is no: Localization seems to be restricted to states rather close to the band edges. However, the mean free path for the extended states is probably not much larger than the intermolecular spacing: The disorder is present uniformly at that scale, and it is not weak.

There are many implications [11] of the scenario described here for the conduction states in doped and undoped C_{60}. In pure C_{60}, momentum selection rules for optical transitions should be violated, and the detailed structure in the energy dependence of the optical absorption near threshold [9] should be washed out. One might also expect to find a thermally activated drift mobility for injected electrons in the conduction band due to the localized states at the band edge; we estimate the activation energy to be about 20 meV for maximal disorder. Less disorder will naturally lead to correspondingly weaker effects. Our present model for disorder does not appear to account for the Urbach edge seen in several spectroscopic studies of thin films [16,17]; but rare, higher-energy configurations of the molecules, producing larger hopping amplitudes, could conceivably yield exponential tails in the density of states.

In the doped materials, the striking difference in $dN(E_F)/dE$ in the orientationally ordered and disordered structures might be evident in the thermopower, which should be much smaller in magnitude in the latter case than in the former, though in both cases it should be p type. Normal-state tunneling may also be able to probe the density of states with sufficient resolution to see the effects of disorder on the density of states. Short mean free paths in the disordered structure could produce high intrinsic resistivity and anomalously fast nuclear spin-

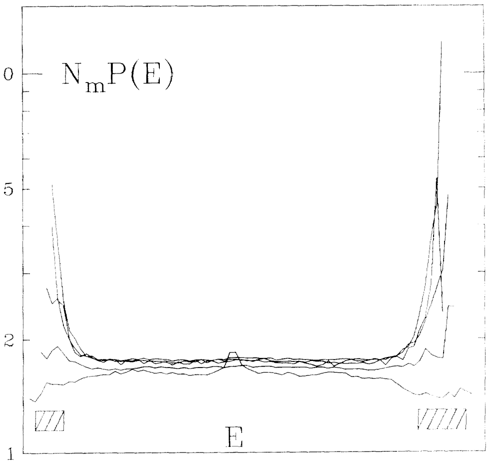

FIG. 5. The participation ratio times the number of molecules vs energy, for the conduction band of the maximally disordered A_3C_{60} structure, for periodic systems of 2^3, 3^3, 4^3, 5^3, and 6^3 cubic cells (corresponding to the five curves, from bottom to top). For delocalized states, that product should approach a finite limit as the system size increases to infinity; such behavior is evident in the center of the band. In the band edges (indicated by the hatched regions) the product appears to increase with system size and thus indicates localization.

lattice relaxation (in comparison with that expected on the basis of the Korringa relation); there is some experimental support for both of these effects [6,18] although the data might be interpreted in other ways. There is also evidence that the superconductivity in Rb_3C_{60} is in the dirty limit [19]; since the coherence length [20] is only tens of angstroms, this is quite consistent with short mean free paths.

In summary, it has been reported experimentally that a specific form of orientational disorder persists at low temperatures in C_{60}, and similar disorder may be intrinsic to the superconducting A_3C_{60} compounds as well. We have determined the effects of such disorder on the conduction-band electronic states by constructing tight-binding models which, for the orientationally ordered structures, reproduce most results of far more sophisticated calculations except for the magnitude of the bandwidth. The densities of states as a function of energy in the disordered systems can be dramatically different from those in the ordered systems although the bandwidth is not changed much. Anderson localization appears to be restricted to the vicinity of the band edges, but the mean free path is likely to be rather short throughout the band.

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