

Effect of molecular orientational disorder on the electronic structure of K_3C_{60}

Raju P. Gupta

Section de Recherches de Metallurgie Physique, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette CEDEX, France

Michèle Gupta

Institut des Sciences des Matériaux, Université de Paris-Sud, Bâtiment 415, 91405 Orsay, France

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The results of electronic structure calculations for the orientationally disordered molecules in K_3C_{60} are presented using the tight-binding recursion method and compared to those in the orientationally ordered state. We find that the electronic densities of states (DOS) in the two cases are quite similar. However, due to a slight broadening of the DOS curve and a shift in the Fermi level (E_F), the value of DOS at E_F is lower in the orientationally disordered structure.

Since the discovery of superconductivity in the alkali-metal-doped C_{60} there has been a considerable effort devoted to the understanding of these molecular solids.¹⁻¹³ Solid C_{60} crystallizes in an fcc (face-centered-cubic) structure at room temperature.¹⁻³ This structure is retained on doping by the alkali-metal atoms K, Rb, Cs for a doping level so that the alkali-metal atoms occupy the previously vacant octahedral and tetrahedral interstitial sites in the fcc lattice, resulting in the formation of the compound A_3C_{60} , where A is an alkali-metal atom (K, Rb, Cs) or a mixture of them. This compound is metallic and superconducting. The superconducting transition temperature T_c depends upon the alkali-metal atoms inserted in the lattice but T_c values of more than 30 K have been obtained⁵ for the compound $RbCs_2C_{60}$.

The C_{60} molecule is formed of a truncated icosahedron which has 20 hexagonal faces and 12 pentagonal faces. This molecule does not possess the full cubic symmetry since, if one aligns the three of its twofold axes along the cubic $\{100\}$ axes, the elements of symmetry related by $\pi/2$ rotations around these axes are missing. This leads to two inequivalent orientations of the molecule (See Fig. 1) in the cubic lattice, each of which could presumably occur with an equal probability. Thus in the alkali-metal-doped compounds A_3C_{60} , the C_{60} molecules are expected to be in an orientationally disordered state. Al-

though the mechanism of superconductivity in these compounds is still not well understood, a correlation has been established between the value of T_c and the lattice parameter of the alkali-metal-doped compound.⁸ On the basis of this correlation it has been suggested that the BCS (Bardeen-Cooper-Schrieffer) theory of superconductivity is applicable for these compounds through the relation $T_c \sim \langle \omega \rangle \exp[-1/VN(E_F)]$, where $\langle \omega \rangle$ is an average phonon frequency, V is an electron-phonon coupling strength parameter, and $N(E_F)$ is the densities of states (DOS) at the Fermi level E_F . Because of the crucial role played by $N(E_F)$ in determining T_c in the BCS relation, it becomes clearly important to know the role which the orientational disorder might play in determining the value of $N(E_F)$.

Recently, several *ab initio* electronic structure calculations⁹⁻¹¹ have been performed for C_{60} and A_3C_{60} . In all these calculations an orientational order, in which all molecules have an identical orientation at the lattice sites, has been assumed considering the complexity of the molecular structure. Satpathy *et al.*¹² recently presented a tight-binding calculation on the effect of the orientational disorder by considering a slab geometry in which alternate $\{100\}$ planes have molecules rotated by $\pi/2$ around the z axis but have an identical rotation in the same plane. Thus in this ordered arrangement each molecule faces four nearest-neighbor molecules which are likewise oriented and eight which are differently oriented. This resulted in a change in the structure in the DOS in the vicinity of the Fermi level in A_3C_{60} and a slight drop in the value of $N(E_F)$ relative to the fully ordered case in which all molecules have the same orientation.

The electronic structure of the completely orientationally disordered A_3C_{60} has been presented by Gelfand and Lu¹³ using also a tight-binding model in which only the three-band complex in the vicinity of the Fermi level was taken into consideration. These authors found, in contrast to the work of Satpathy *et al.*,¹² that the orientational disorder washes out completely the structure in the DOS not only in the vicinity of the Fermi level but in the entire three-band complex; the DOS in the three-band complex in the conduction band was found to be almost flat over the entire energy range. However, their compu-

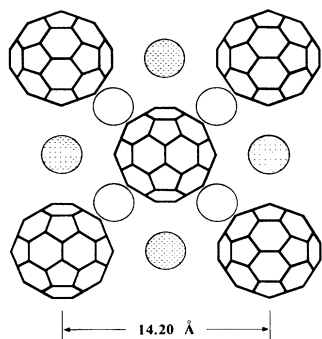


FIG. 1. Crystal structure of K_3C_{60} . Filled and open circles represent K atoms in octahedral and tetrahedral positions, respectively.

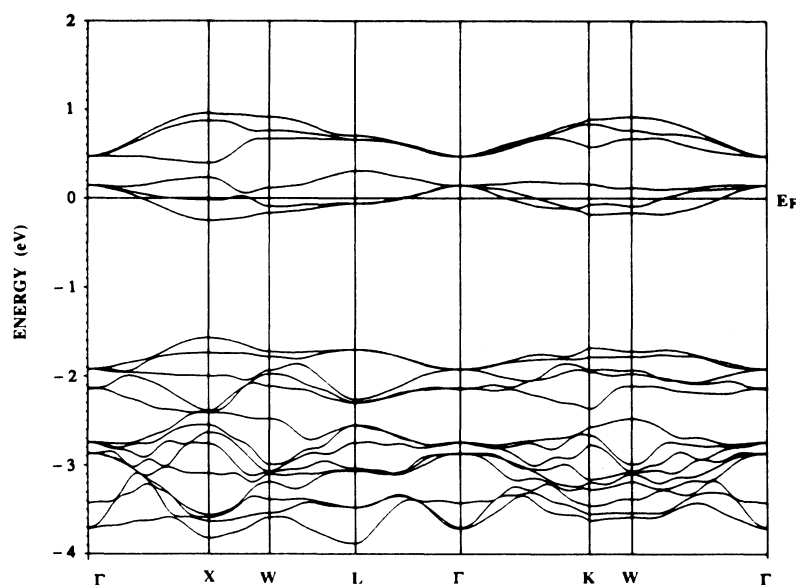


FIG. 2. Band structure of K_3C_{60} in the orientationally ordered state along several symmetry directions. The Fermi level E_F is located at the zero of the energy scale.

tional procedure also results in the tight-binding parameters that yield a bandwidth and an energy gap between valence and conduction bands an order of magnitude too small relative to those found in other calculations.

In this paper, we present the results of our electronic structure calculations for the orientationally disordered C_{60} using the tight-binding recursion method. This method offers an inherent advantage over other methods for treating the disordered systems since it is a real-space technique and requires no periodicity, in contrast to the *ab initio* reciprocal space methods which depend upon the use of the Bloch's theorem. Furthermore, there is no restriction on the basis set for the expansion of the wave function, and the DOS in the whole range of energy are obtained. In this method the DOS are calculated directly at individual atomic sites through the recursion technique, amounting essentially to an outward integration. A given atom interacts directly with its neighbors which in turn interact with theirs, leading to an indirect interaction of the the central atom with distant neighbors. This technique has been described in detail elsewhere,¹⁴ where a complete exposition of the mathematical formulation has been given. In our calculation, both $2s$ and $2p$ wave functions at the carbon sites were included, and the tight-binding parameters were taken from the work of Tomanek and Schluter¹⁵ on carbon clusters with the values $E_s = -7.3$ eV and $E_p = 0.0$ eV for the diagonal elements, and $ss\sigma = -3.63$ eV, $sp\sigma = 4.20$ eV, $pp\sigma = 5.38$ eV, and $pp\pi = -2.24$ eV for the hopping integrals corresponding to a C-C separation $d = 1.546$ Å, which is the equilibrium nearest-neighbor distance in diamond. A $1/d^3$ distance dependence of the hopping parameters was assumed since it has been suggested¹⁶ that it is more appropriate for this class of materials and since it also yields a band gap in the orientationally ordered C_{60} in good agreement with other calculations.⁹⁻¹¹ In our calculations we restricted, following Satpathy *et al.*,¹² the interaction of a C atom to its first three nearest-neighbor C atoms in constructing intramolecular matrix elements.

On the other hand, all C neighbors within a distance of ~ 5.2 Å were included for interactions between molecules. As a first approximation, all C bond lengths were assumed to be equal (1.42 Å) and we neglected the slight difference that exists between different bonds, although actual bond lengths could have been used without any difficulty.

The calculations were performed for C_{60} with an fcc lattice parameter $a = 14.20$ Å, and K was assumed to be fully ionic, as found in previous calculations.⁹⁻¹¹ The tight-binding recursion method, to our knowledge, has never been used before for such large molecular systems. In order to provide a reference frame for comparison and also to test the accuracy of the tight-binding parameters, energy band dispersion curves were calculated for the fully orientationally ordered K_3C_{60} by the usual reciprocal space method. These are shown in Fig. 2 and are in good agreement with other calculations.⁹⁻¹¹ The width of the conduction band is found to be ~ 0.5 eV and the energy gap between the valence and conduction band ~ 1.5 eV, in good agreement with previous work.⁹⁻¹¹ DOS were then calculated using the usual tetrahedron method¹⁷ with an initial mesh of 89 points in the irreducible $\frac{1}{48}$ portion of the Brillouin zone (IBZ) and a total of ~ 6600 tetrahedrons in the IBZ. This DOS curve, slightly broadened with a Gaussian with half width at half maximum (HWHM) of $\sigma = 0.02$ eV is shown in Fig. 3, and is also in good agreement with previous calculations.⁹⁻¹¹

In our calculations by the recursion method, to be described below, a cluster of 256 C_{60} molecules (15 360 carbon atoms) located on a regular fcc lattice was used. Considering the fact that the molecule contains a significant amount of hollow space in the center, a large number of recursions were found to be necessary to correctly reproduce the structure in the DOS found in Fig. 3. The DOS obtained with the recursion method with 190 recursions is shown in Fig. 4 for the case of fully orientationally ordered C_{60} . This DOS curve has been broadened with a Gaussian with $\sigma = 0.05$ eV. Compar-

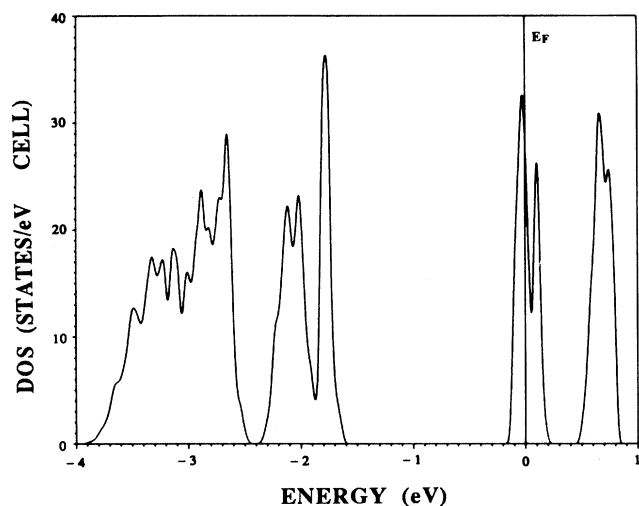


FIG. 3. Densities of states (DOS) for K_3C_{60} in the orientationally ordered state obtained using the tetrahedron method. The Fermi level E_F is located at the zero of the energy scale.

sion of Fig. 4 with Fig. 3 shows that the recursion method reproduces quite reasonably the DOS obtained with the usual reciprocal space method. In particular, the structure of the peaks in the DOS, their positions, and their heights are approximately the same in the two DOS curves. We obtain a value of $N(E_F)=27.98$ states/eV molecule for both spins for K_3C_{60} with the reciprocal space method and 25.72 states/eV molecule with the recursion method. These values are in good agreement with other calculations.⁹⁻¹²

In our calculation, the orientational disorder was simu-

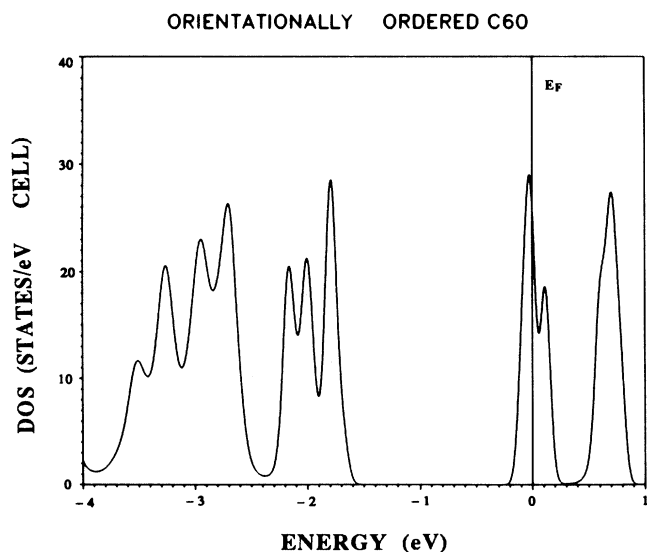


FIG. 4. Densities of states for K_3C_{60} in the orientationally ordered state obtained using the tight-binding recursion method. The Fermi level E_F is located at the zero of the energy scale.

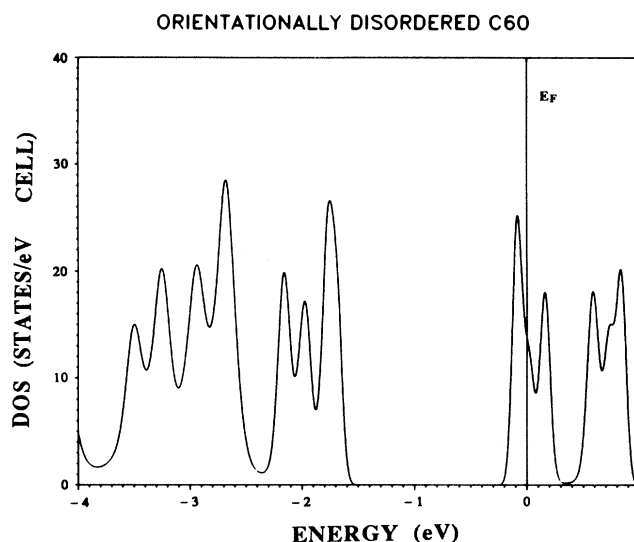


FIG. 5. Densities of states for K_3C_{60} in the orientationally disordered state obtained using the tight-binding recursion method. The Fermi level E_F is located at the zero of the energy scale.

lated by placing the two possible orientations of the molecule at random in a manner so that each molecular orientation has an equal probability of occurrence. The DOS for this orientationally disordered structure (broadened with a Gaussian with $\sigma=0.05$ eV) is shown in Fig. 5. Comparing Fig. 5 with Fig. 4, one notices a rather striking similarity in the two electronic structures in the orientationally ordered and disordered forms. Except for some structure that was present in the orientationally ordered form at energies higher than 0.5 eV (formed by the second triply degenerate conduction band) that has been washed out in the orientationally disordered form, all major features in the vicinity of the Fermi level and below have remained intact. The valence and conduction band edges remain sharp and the band gap remains unaffected due to orientational disorder. Structurally speaking, the orientationally disordered form of C_{60} can be considered to be quite analogous to that of amorphous SiO_2 where in contrast to fixed bond lengths and bond angles found in α -quartz, there is a statistical distribution around these values. This results in some smoothing out of the fine structure in DOS in amorphous SiO_2 compared to that in α -quartz, but on the whole the two electronic structures are quite similar.¹⁸ Similarly, orientational disorder in C_{60} does not affect the essential features of the electronic structure in the orientationally ordered state, except that there is some broadening of peaks. This results in a slight shift in the position of the Fermi level and a reduced value of the DOS at E_F in K_3C_{60} . We obtain a value of $N(E_F)=13.54$ states/eV molecule in the orientationally disordered state.

In conclusion, our electronic structure calculations have shown that the electronic structure of K_3C_{60} in the orientationally disordered state of C_{60} molecules is, on

the whole, quite similar to the one in the orientationally ordered state. However, there is a slight broadening of the structure in the DOS due to a different distribution of the C-C bond lengths between molecules in the orienta-

tionally disordered state. This leads to a small shift in the Fermi level and a reduction in the value of $N(E_F)$ since the Fermi level E_F falls in a rapidly falling portion of the DOS curve.

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