

Electronic structure of orientationally ordered and disordered K_3C_{60}

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The C_{60} molecule does not have 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 in the cubic lattice, each of which could occur with an equal probability. We have performed the electronic structure calculations for K_3C_{60} for the orientationally disordered C_{60} molecules 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 does not require periodicity. Our calculations show that the electronic densities of states (DOS) in the orientationally disordered state are quite similar to those in the orientationally ordered state. 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.

1. INTRODUCTION

There has been considerable interest in the study of the electronic properties of C_{60} since the discovery of superconductivity in these compounds induced by alkali doping. Solid C_{60} crystallizes in an fcc structure at room temperature and this structure is retained on doping by the alkali atoms K, Rb, Cs. These elements occupy the octahedral and tetrahedral interstitial sites in the lattice, resulting in the formation of the compound A_3C_{60} , where A is an alkali atom. The C_{60} molecule is formed of a truncated icosahedron which has 20 hexagonal faces and 12 pentagonal faces and 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 in the cubic lattice, as shown in Fig. 1, each of which could 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 [1].

Several *ab initio* electronic structure calculations [2-4] have recently 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 all lattice sites, has been assumed due to the complexity of the molecular structure. The electronic structure of the completely orientationally disordered A_3C_{60} has been recently presented by Gelfand and Lu [5] using a

tight binding model in which only the t_{1u} band complex in the vicinity of the Fermi level, E_F , was taken into consideration. These authors found that the orientational disorder has a drastic effect on the densities of states (DOS) and that the fine structure and peaks present in the orientationally ordered state were replaced by a flat DOS in the orientationally disordered state. These calculations are in disagreement with those of Satpathy et al. [6] who, also using a tight binding model but with a slab geometry to simulate orientational disorder in which alternate [100] planes have molecules rotated by $\pi/2$ around the z-axis, found only a slight modification in the structure in the DOS in the vicinity of E_F , and a slight drop in $N(E_F)$, the value of DOS at E_F . In this paper the results of our electronic structure calculations are presented which make no approximation concerning the nature of disorder and include all electronic states relevant to the C_{60} molecule.

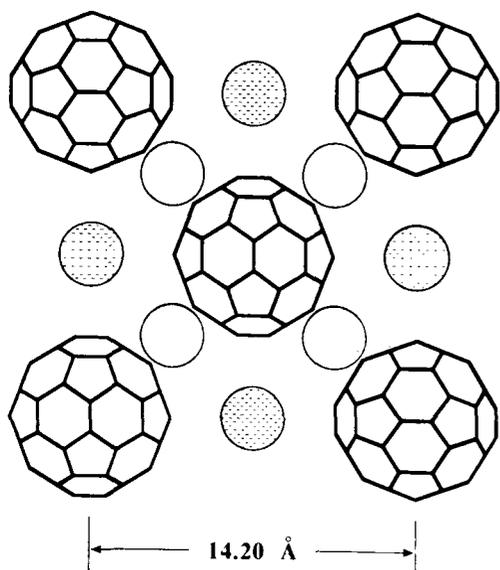


Fig. 1 : Crystal structure of K_3C_{60} . Filled and open circles represent K atoms in octahedral and tetrahedral positions respectively.

2. DETAILS OF CALCULATION

The electronic structure calculations were performed using the tight binding recursion method [7] which is inherently advantageous over other methods for treating disorder. This is a real space technique and requires no periodicity in the structure, 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 wavefunctions, and the DOS in the whole energy range are obtained. The DOS in this method 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 interacts with theirs, leading to an indirect interaction of the central atom with distant neighbors. In our calculation both 2s and 2p wavefunctions at the carbon sites were included. The on-site energies and transfer integrals were taken from the work of Tomanek and Schluter [8] on carbon clusters, and a $1/d^3$ distance dependence of the hopping parameters was assumed since it has been suggested [9] that it is more appropriate for this class of materials, and also since it yields a band gap in the orientationally ordered C_{60} in good agreement with other calculations. The interaction of a C atom were restricted to its first three nearest C neighbors on the same C_{60} molecule but all C neighbors within a distance of ~ 5.2 Å were included in intermolecular interactions. The calculations were performed with an fcc lattice parameter $a = 14.20$ Å, and K was assumed to be fully ionic, as found in previous calculations [2-4].

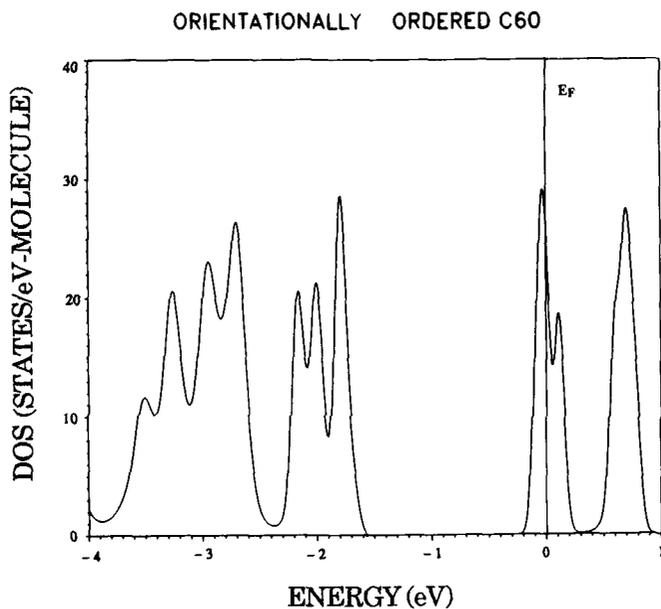


Fig. 2 : Densities of states for K_3C_{60} in the orientationally ordered state. The Fermi level E_F is located at the zero of the energy scale.

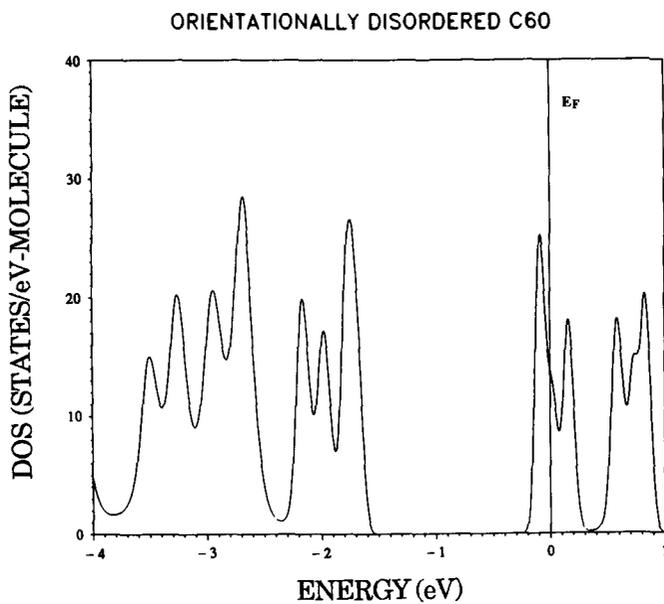


Fig. 3 : Densities of states for K_3C_{60} in the orientationally disordered state. The Fermi level E_F is located at the zero of the energy scale.

3. RESULTS AND DISCUSSION

A cluster of 256 C₆₀ molecules (15360 carbon atoms) located on a regular fcc lattice was used in our calculation. 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 obtain accurate DOS. The DOS obtained with the recursion method with 190 recursion is shown in Fig. 2 for the case of fully orientationally ordered C₆₀. This curve has been broadened with a Gaussian with the half width at half maximum $\sigma = 0.05$ eV. The orientational disorder was simulated 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 also with a Gaussian with $\sigma = 0.05$ eV) is shown in Fig. 3. If we compare Fig. 3 with Fig. 2 we see that the electronic structure in the orientationally disordered state is strikingly similar to the one in the orientationally ordered state. This is in contrast to the result that was obtained by Gelfand and Lu [5] but in agreement with the recent work by Shirley and Louie [10]. Except for some structure that was not present at energies ~ 0.5 eV above the Fermi level formed by the t_{1g} conduction band, all major features in the vicinity of the Fermi level and below have remained fully intact. The valence and conduction band edges remain sharp and the band gap remains unaffected by the orientational disorder. Structurally speaking, the orientationally disordered form of C₆₀ can be considered to be quite similar to that of amorphous SiO₂ where in contrast to the fixed bond lengths and bond angles found in crystalline quartz, there is a statistical distribution around these values. This results in some smoothing out of the fine structure in DOS in amorphous SiO₂ compared to that in

crystalline quartz but on the whole the two electronic structures [11] are quite similar. The C-C bond lengths between the two C₆₀ molecules of opposite orientations are not the same as between those of the same orientations but rather vary around these values. Thus similar to the case of amorphous SiO₂ the orientational disorder in C₆₀ does not affect the essential features of the electronic structure found in the orientationally ordered state, except that there is some broadening of the 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 K₃C₆₀ since the Fermi level in this compound falls in a rather rapidly varying portion of the DOS curve. We obtain a value of $N(E_F) = 13.54$ states/eV molecule in the orientationally disordered state compared to a value of $N(E_F) = 25.72$ states/eV-molecule in the orientationally ordered state.

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