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journal homepage: www.elsevier.com/locate/cplettThe effect of structural changes on ELNES for C₆₀R.J. Nicholls^{a,*}, D. Nguyen-Manh^b, D.J.H. Cockayne^a, S. Lazar^{c,1}^a Department of Materials, University of Oxford, Parks Road, Oxford, Oxfordshire OX1 3PH, UK^b EURATOM/UKAEA Fusion Association, Culham Science Centre, Abingdon OX14 3DB, UK^c Kavli Institute of Nanoscience, Delft University of Technology, Lorentzweg 1, 2628CJ Delft, The Netherlands

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ABSTRACT

The unoccupied density of states is simulated for two different experimentally determined C₆₀ crystal structures. Several theoretical crystal structures are constructed to allow the effects of bond length and relative molecular orientation to be studied. It is found that both have an effect on the unoccupied states, and that the larger effect is coming from the variation in bond length. It is suggested that the difference previously reported in the electron energy loss spectra from C₆₀ thin films and nanocrystals could be due to differences in bond length, if these differences in bond length are sufficiently large.

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1. Introduction

Carbon nanostructures, such as fullerenes and nanotubes, are currently the focus of considerable research, because of their potential use in a wide variety of nano-systems such as for drug delivery [1], as qubits in a quantum computer [2] and as transistors [3]. Many of these applications depend upon properties determined by their physical and electronic structure. Information about the electronic structure can be obtained from electron energy loss (EEL) spectroscopy, because it provides information about the unoccupied density of states (DOS).

It has been reported that the EEL spectra from C₆₀ thin films differ from that obtained from C₆₀ nanocrystals [4], and so the question arises as to what in the structure is responsible for these differences. In order to investigate the key parameters which influence the shape of the EEL spectra, the unoccupied DOS is simulated for several model C₆₀ structures based upon two different experimentally determined C₆₀ structures as reported by Dorset and McCourt [5,6] and by David et al. [6,7]. The structure determined by Dorset and McCourt [5], from the analysis of room temperature electron diffraction intensity data, is fcc with four C₆₀ molecules in the unit cell. The space group is *Fm* $\bar{3}$ with lattice parameter 1.426 nm, and there are three inequivalent atoms in the unit cell. This structure is shown in Fig. 1a and will be referred to as the F1 structure. In contrast to the generally accepted view that the C₆₀ molecules would be rotating at room temperature, the molecules in this model are static. The authors commented that this is an artefact caused

by a limited number of phased structure factors in the analysis, and that the data itself is not inconsistent with the view that there is no angular correlation between the molecules. It would be very difficult to model spectra from a crystal with rotating C₆₀ molecules due to the large number of spectra that would need to be simulated and averaged, and so this model is taken as a useful starting point.

The structure determined by David et al. [7], from a low temperature neutron powder diffraction study, is primitive cubic, with four molecules in the unit cell and ten inequivalent atoms. The space group is *Pa* $\bar{3}$ with lattice parameter 1.404 nm. This structure is shown in Fig. 1b and will be referred to as the C1 structure.

2. Computational details

Simulations of the DOS of the structures were performed using density functional theory within the LDA approximation by the WIEN2k package [8]. The value of *RK*_{max} (the product of the atomic sphere radius and the plane wave cut off) used to simulate the DOS was 5.5. Simulations were carried out for the less computationally intense F1 structure with different values of *RK*_{max} and it was found that 5.5 was small enough to allow the simulation of such large systems without affecting the accuracy of the results obtained. A 4 × 4 × 4 k-mesh has been used for all the calculations shown here. This corresponds to a k-mesh spacing of 0.18 nm⁻¹ in both the F1 and C1 cases. This k-mesh was found to be dense enough to produce an accurate DOS by varying the k-mesh for the F1 structure. The DOS was calculated for each type of inequivalent atom in the structure and then averaged, taking into account the number of each type of inequivalent atom in the unit cell [9]. All structures are crystalline, and this work is a natural extension of previous work on C₆₀ molecules (e.g. [10]).

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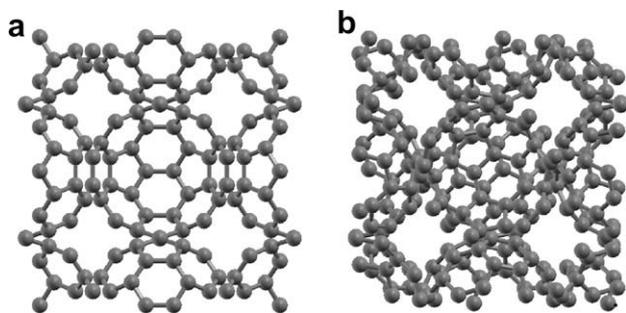


Fig. 1. The F1 (a) and C1 (b) unit cells viewed along [001].

3. Results and discussion

Simulated DOS from the F1 and C1 structures are shown in Fig. 2. The DOS is shown up to 3 eV above the lowest unoccupied molecular orbital (LUMO), as this part of the DOS corresponding to the region of the EEL spectrum where differences have been observed experimentally between C₆₀ samples [4]. The C1 DOS shows a more complicated splitting of states than F1 in the first 2 eV above the LUMO, and in order to understand the cause of this we need first to consider the differences between the two structures themselves. There are three parameters: (1) Unit cell size: both structures have a cubic unit cell, but with the lattice parameter of F1 being 1.426 nm and of C1 being 1.404 nm. (2) Bond lengths: in F1 the bond lengths vary from 0.146 nm to 0.148 nm, while in C1 the variation is from 0.137 to 0.148 nm. (3) Relative orientation: in F1 all the molecules are oriented the same way, while in C1 there is a rotation of the molecule at the origin of the unit cell of approximately 98° anticlockwise around the [111] orientation. This causes a rotation of all the molecules to produce the cubic unit cell.

In order to consider the effect of these three parameters on the DOS, the lattice parameters were made equal by setting the F1 lattice parameter to that of C1. The resulting model is referred to as F1* – the C₆₀ molecules have the same orientation and bond lengths as in F1. There was found to be a small difference in the DOS simulated from F1 and F1*, as seen in Fig. 3a.

To assess the effects of differences in the bond length and molecule orientation on the DOS, two new unit cells were constructed. The first (F2) was an fcc unit cell with the same lattice parameter, space group and molecule orientation as F1*, but with the C₆₀ molecule replaced with an ideal C₆₀ molecule obtained from the Computational Chemistry List, which has only two different bond lengths. This means that the only differences between the F1* and F2 are the bond lengths. The second (C2) was a primitive cubic unit cell with the same ideal C₆₀ molecule as F2, and with the same

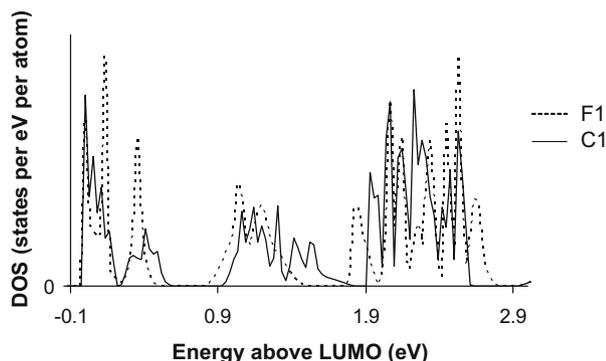


Fig. 2. DOS up to 3 eV above the LUMO for the F1 and C1 structures.

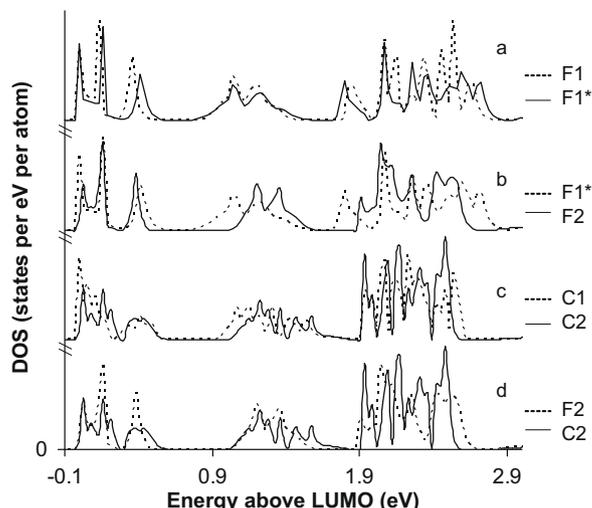


Fig. 3. DOS up to 3 eV above the LUMO for the F1, F1*, F2, C1 and C2 structures.

lattice parameter, space group and molecular orientation as C1. The only difference between C1 and C2 is the bond lengths, and the only difference between F2 and C2 is the orientation of the molecules. The differences between all the structures are summarised in Fig. 4.

Fig. 3 shows the calculated DOS from F2 and C2, alongside the DOS from F1* and C1. The largest change in DOS when considering the variation in lattice parameter, bond length and relative orientation separately, is between F1* and F2. This difference is as a result of the variation in bond lengths between the two structures. The change in the DOS between the F1* and F2 structures is not as large as the difference between the experimentally determined structures F1 and C1 and Fig. 3 shows that the orientation of the molecules also has an effect. The result (that the effect of the variation in the bond lengths within the molecule is larger than the effect of orientation of the molecules on the DOS) is in agreement with the previous finding that the effect of the environment of a fullerene molecule on the spectra obtained from X-ray absorption experiments is small [11].

As when comparing F1* and F2, the only differences when comparing C1 and C2 are the bond lengths. The bond lengths in C2 and F2 are the same, 0.137 and 0.145 nm. The bond lengths in the C1 structure vary between 0.137 and 0.148 nm, whilst in the F1*

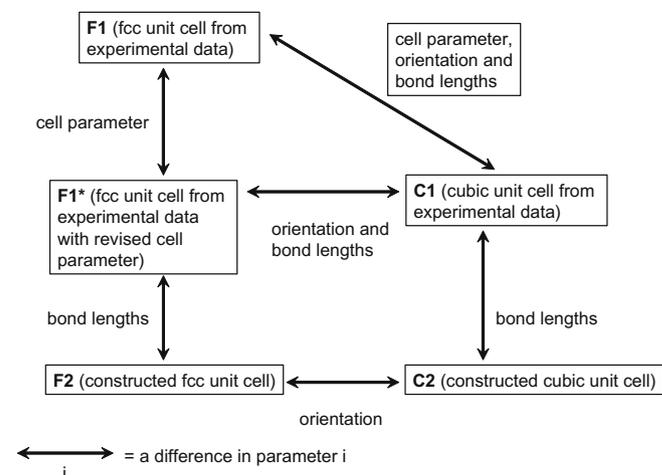


Fig. 4. Summary of the differences between the F1, F1*, F2, C1 and C2 structures.

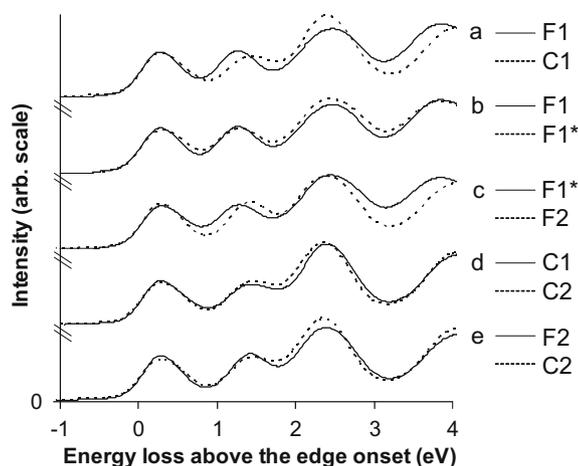


Fig. 5. Simulated spectra from the F1, F1*, F2, C1 and C2 structures.

structure they vary between 0.146 and 0.149 nm. In the C1 structure, 60% of the bond lengths are between 0.137 and 0.145 nm, whilst none of the F1 bond lengths are. The variation between the bond lengths is greater when comparing F1* and F2 than when comparing C1 and C2 and a larger variation in the DOS is seen.

3.1. Electron energy loss spectra

While we have investigated the effects of bond length variations and molecular orientation on the DOS, it is not evident whether the resulting differences in the EEL spectra would be sufficiently large to probe by EELS. In order to investigate this, EEL spectra simulations were carried out for all of the structures. The calculations were performed using the TELNES2 part of the WIEN2k package. The spectra were simulated for a polycrystalline sample, with an electron beam energy of 120 keV and an instrumentation broadening of 0.3 eV. Lifetime broadening effects were taken into account, but core-hole effects were not included due to the size of the supercell which would need to be created.

Fig. 5 shows the simulated spectra from the F1, F1*, F2, C1 and C2 structures. The spectra are shown up to 4 eV above the edge onset, as this is the region which shows the critical features important to this study.

There is a difference between the spectra from the F1 and C1 structures in both the positions and intensities of the three peaks, which are at 0.3, 1.2 and 2.5 eV in the F1 case and 0.3, 1.4, and 2.4 eV in the C1 case. It can be seen that the changes between the two structures which lead to a more complicated splitting of the DOS has in turn caused a change in the positions and relative heights of the peaks in the EEL spectrum. The differences between the other structures are all smaller than the variation between the F1 and C1 structures as expected from the simulated DOS.

It has to be recognised, however, that while the simulated C1 and F1 EEL spectra show differences, these small differences would be difficult to distinguish conclusively using experiment. Of course, the core-hole will affect the intensities of the peaks but simulations of spectra which include the effect of the core-hole are very difficult because of the size of the supercell which would need to

be constructed [9]. This effect is not important in this discussion because (1) it is expected to effect the ELNES of all models in a similar way and (2) we are not trying to reproduce experimental data.

If it is unlikely that the differences in the structures considered here could be distinguished experimentally, it may be that there are cases in which, for example, the bond lengths are changed enough for the effect to be detected in the EEL spectrum. For example since the C₆₀ nanocrystals mentioned above were forced quickly out of solution, solvent molecules or impurities might remain within the C₆₀ lattice, causing significant changes in the bond lengths within the molecules. Of course, to separate out the effects on bond length from other effects (e.g. chemical environment) which might influence the spectrum would be difficult. Another possibility is that any dimerisation or polymerisation of the C₆₀ molecules could cause a change in the bond lengths. EEL spectra from C₆₀ dimers and polymers have been obtained by several groups [12,13] and the spectra fit in well with the differences observed here. Studies which compare EEL spectra from different C₆₀ crystals unfortunately do not show spectra of high energy resolution to compare the simulated spectra to.

4. Summary

In conclusion, the analysis reported here shows that changes in the C₆₀ crystal structure can have an effect on the DOS; that, if these differences are sufficiently large, their effect could be observed in experimental EEL spectra; and that structural changes, for example differences in bond length, if sufficiently large, could account for the reported differences between EEL spectra from C₆₀ films and nanocrystals.

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References

- [1] H. Shinohara, Rep. Prog. Phys. 63 (2000) 843.
- [2] G.A.D. Briggs, Patent Number WO03007234, 2003.
- [3] T. Shimada et al., Jpn. J. Appl. Phys. 44 (2005) 469.
- [4] S.M. Lee, R.J. Nicholls, D. Nguyen-Manh, D.G. Pettifor, G.A.D. Briggs, D.A. Pankhurst, D.J.H. Cockayne, Chem. Phys. Lett. 404 (2005) 206.
- [5] D.L. Dorset, M.P. McCourt, Acta Cryst. A50 (1994) 344.
- [6] D.A. Fletcher, R.F. McMeeking, D. Parkin, J. Chem. Info. Comp. Sci. 36 (1996) 746.
- [7] W.I.F. David et al., Nature 353 (1991) 147.
- [8] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Karlheinz Schwarz, Techn. Uni. Wien, Austria, 2001. ISBN 3-9501031-1-2.
- [9] R.J. Nicholls, D.Phil. Thesis, University of Oxford, 2006.
- [10] A.A. El-Barbary et al., J. Phys. Conf. Series 26 (2006) 149.
- [11] L.J. Terminello, D.K. Shuh, F.J. Himpsel, D.A. Lapiano-Smith, J. Stohr, D.S. Bethune, G. Meijer, Chem. Phys. Lett. 182 (1991) 491.
- [12] M. Terauchi, S. Nishimura, Y. Iwasa, J. Electron Spectrosc. Relat. Phenom. 143 (2005) 169.
- [13] M. Sing, A. Soldatov, T. Pichler, B. Sundqvist, M. Knupfer, M.S. Golden, J. Fink, Syn. Metals 103 (1999) 2454.