Modelling of crystalline C$_{60}$ EEL spectra

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Abstract. Electron energy-loss spectra are simulated from two experimentally determined C$_{60}$ crystal structures. It is found that the decrease in symmetry from a face centred cubic to a simple cubic structure cause a splitting of the unoccupied states resulting in a splitting and broadening of the peaks in the spectrum and a change in the relative heights of those peaks. The simulated spectra are then compared to experimental spectra from C$_{60}$ thin films and nanocrystals.

1. Introduction
Since their discovery in 1985 [1], fullerenes have been intensively studied in order to better understand their properties and increase their potential applications. One way the electronic properties of these molecules can be probed is by using electron energy loss (EEL) spectroscopy. The spectra produced can be interpreted with the help of density functional theory calculations.

We have previously obtained EEL spectroscopy data from C$_{60}$ nanocrystalline samples [2]. The spectrum was found to differ from that obtained by other groups from thin films [3]. The difference has been previously ascribed to the different sample preparation methods used [4]. In this paper, we simulate EEL spectra from two different C$_{60}$ crystal structures for comparison with the experimental data.

2. Method
The simulations were performed using density functional theory with a LDA functional by the WIEN2k package [5]. Two previous experimentally determined crystal structures were used for the simulations. The first was determined at room temperature from electron diffraction intensity data [6]. The deduced structure was face centred cubic (fcc) with four C$_{60}$ molecules in the unit cell and three inequivalent atoms. The lattice parameter is 1.426nm and the space group is Fm3-. The molecules in the model unit cell are static, but the authors comment that this was an artefact caused by using a limited set of phased structure factors in the analysis, although the data itself shows that there is no strong correlation of angular orientation between molecules in the unit cell. Consequently it would not be inconsistent with the work of Dorset and McCourt to use their fcc model, but with the molecules rotating. It is, however, very difficult to model spectra from a crystal with rotating C$_{60}$ molecules, and so a static fcc structure is a good place to start. The second structure used is from a low temperature neutron powder diffraction study [7]. The structure is similar to the fcc structure, but with the four C$_{60}$ molecules not in identical orientations, so that a simple cubic (sc) structure results with ten inequivalent atoms. This unit cell has lattice parameter 1.404nm and space group Pa3-. The unit cells for the two structures are shown in Figure 1. The lattice parameters of the two structures differ by
0.02 nm and the range of nearest neighbour distances for the fcc structure is 0.146-0.148 nm compared with 0.137-0.141 nm for the sc structure.

The calculations were carried out using an atomic sphere radius of 1.3 a.u. for the fcc case and 1.29 a.u. for the sc case. The calculation for the fcc structure was carried out with values of the fundamental parameter $R_{\text{K\text{MAX}}}^\text{MAX}$ between 5 and 7 but it was found that the value used had little effect on the simulated EEL spectra. The results shown here are for $R_{\text{K\text{MAX}}}^\text{MAX} = 7$. The calculation of the sc structure was larger in terms of computer memory, as there are more inequivalent atoms in the unit cell. As a result, only a calculation with $R_{\text{K\text{MAX}}}^\text{MAX} = 5.5$ was carried out. The number of k-points used to sample the irreducible Brillouin Zone was 18 in the fcc case and 4 in the sc case. This gives k-mesh spacings of $0.12\text{nm}^{-1}$ and $0.18\text{nm}^{-1}$ respectively. The EEL spectra simulations were performed using the WIEN2k package, using the TELNES program with includes the transition matrix element. The spectra were simulated for a polycrystalline sample rather than a specific orientation by integrating over a sphere and an electron beam energy of 120kV was used.

Figure 1: The structure of (a) fcc and (b) sc $C_{60}$ crystal lattices viewed looking down the c axis.

3. Results and Discussion

Figure 2 shows the simulated spectra produced from the two structures. Lifetime broadening has not been taken into account, and so there are many peaks at energies above about 5eV which would not be distinguishable in an experimental spectrum. Core-hole broadening has also not been taken into
account, and the effect of the core-hole on the spectrum is to be investigated in further work. It can be seen that the two crystal structures produce different simulated EEL spectra. As we are interested in those features which can be seen in an experimental spectrum, the main difference between the two spectra that we concentrate on is the relative heights of the first three peaks. We note that the spectrum for the fcc structure is similar to the unoccupied density of states of a $\text{C}_{60}$ molecule [4].

In Figure 3, the simulated spectra are separated into contributions from the different types of inequivalent atom. It can be seen that the change from an fcc to a sc structure has caused splitting of the peaks. By considering the detailed (unbroadened) unoccupied DOS in the energy range 0-3eV shown in Figure 4, we can see that a lowering of the symmetry as we move from an fcc to a sc structure causes a more complicated splitting of states. This splitting has caused broadening and splitting of peaks in the EEL spectrum as well as a change in the relative heights of the peaks.

**Figure 3:** The contribution to the simulated spectra from each of the inequivalent atoms in both the fcc and sc structures.

**Figure 4:** The unbroadened DOS (per atom) from each of the inequivalent atoms in both the fcc and sc structures.

Experimental spectra in the literature from thin films show two clear peaks near to 1.6 and 2.2 eV above the edge onset [3]. These spectra are better described by the simulated spectrum produced from the fcc structure. Experimental spectra from nanocrystals [2] show one very broad peak at 2 eV above the edge onset. This spectrum is a better match to the simulated spectrum from the sc structure. These
matches suggest that the different sample preparation methods may produce different crystal structures. However, these results raise the question of why the experimental data from a room temperature fcc rotating C_{60} crystal, with no correlation of angular position (as in the thin film) matches well with a static fcc model in which all molecules are oriented the same way. This question remains under investigation.

4. Summary
We have shown that EEL spectra simulated from two different experimentally determined C_{60} crystal structures are different. Experimental EEL spectroscopy data from thin films is similar to that simulated from the fcc structure, whilst the experimental spectra from nanocrystals is similar to that simulated from the sc case. These observations are under further investigation, including a deeper analysis of theoretical results.

5. Acknowledgements
RN would like to thank St. Catherine’s College, Oxford and the EPSRC for financial support.

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