Chapter 7

Further Work

The work presented in this thesis has been in two parts. The first part has investigated the possibility of using simulated spectra to relate the significant features in EEL spectra from C_{60} and C_{70} to aspects of model structures. The second part has investigated EEL spectra from endohedral fullerenes Nd@C_{82} and Sc_3N@C_{80}.

The possible of further work to extend this investigation is discussed here.

7.1 Core-hole effects

Core-hole effects have not been taken into account in any of the simulation of the spectra shown in Chapters 4 and 5. Calculations on graphite carried out in Chapter 3 showed that this effect could be important. In order to take the core-hole effects into account for any of the C_{60} or C_{70} structures, a core-hole calculation would need to be carried out for each of the inequivalent atom positions. The largest spacing of equivalent atoms in any of the C_{60} structures is 0.45 nm. In Chapter 3 it was found that, for graphite, core-holes with a spacing of 0.49 nm interact with each other. This means that

supercells would need to be created for the C_{60} structures to prevent core-hole interactions.

For C_{70}, there are 40 inequivalent atoms. Some of these atom types have distances of 0.24 nm between them, whilst others have distances of 0.89 nm, and so only some of the atoms would require the construction of supercells. As 40 separate self-consistent calculations would need to be carried out, with the computer available, this would take almost three years. This is not possible with the time available here, but in order to gauge the effects of the core-hole, one calculation has been carried out on an atom which does not require a supercell, to see the effect of the core-hole on the spectrum from one of the atoms.

The atom used in this calculation is one of the atoms from ring e in Figure 5.10b. This atom is a distance of 0.89 nm from the nearest equivalent atom. In Chapter 3 it was found that for graphite a distance of 0.98 nm was enough to stop core-hole interactions which were seen at a distance of 0.49 nm. The core-hole calculation was carried out by removing one of the core electrons and adding it into the valence band. The effect of the core-hole on the EEL spectrum contribution from this atom can be seen in Figure 7.1. The figure shows that the core-hole does have an appreciable effect on the near-edge structure. There is an enhancing of the peak at the edge onset and the levels have been pulled down towards the Fermi level. Figure 7.2 shows the DOS for both cases.

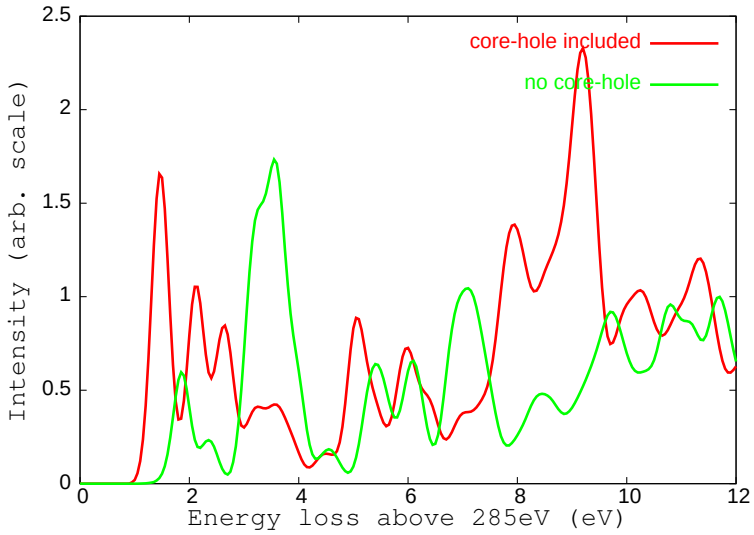


Figure 7.1: The EEL spectrum contribution from one of the atoms calculated with and without core-hole effects

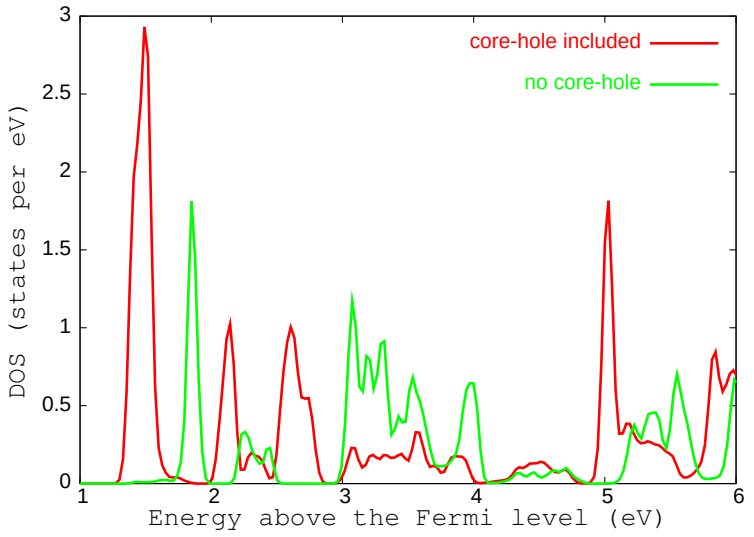


Figure 7.2: The DOS from one of the atoms calculated with and without core-hole effects

The contributions to the spectrum from the atom with and without the core-hole are compared to the experimental EEL spectrum obtained from the C_{70} nanocrystals in Figure 7.3. The experimental spectrum (7.3a) and the total simulated C_{70} EEL spectrum (7.3b) have been aligned using the edge onsets. The contribution to the total EEL spectrum from the atom does not have the same onset as the total spectrum, and so it is displayed shifted with respect to the total spectrum. The core-hole spectrum is shifted with respect to the non core-hole calculation, and so it is difficult to align with the other spectra. It has been aligned using the maximum of the first peak with the non core-hole contribution.

This core-hole calculation has shown that including a core-hole can have an effect on the contribution of an individual atom to the EEL spectrum. It is likely that the total EEL spectrum for a complete core-hole calculation would be different to that from the non core-hole calculation calculated here[1]. It is not possible, however, to predict what shape that EEL spectrum may take.

As the contribution to the total C_{70} spectrum from all atoms within one ring is similar, to get an approximation to a full core-hole calculation, five of the atoms, one in each ring, could be used for core-hole calculations. Here a calculation has been carried out for an atom where it was not necessary to construct a supercell. This is not the case for atoms in all of the rings, and so in order to proceed with this core-hole investigation, the next step would

[1]It is unlikely that inclusion of a core-hole would account for the differences seen in Chapter 4 between the experimental data from the C_{60} thin films and nanocrystals as the effect of the core-hole should be similar in both samples.

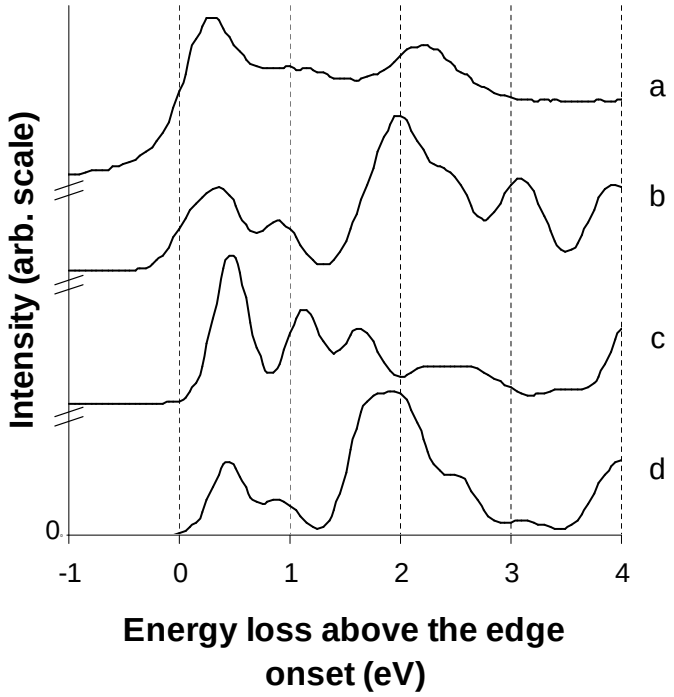


Figure 7.3: Experimental nanocrystalline C_{70} EEL spectrum (a), total simulated C_{70} EEL spectrum (b) and the contribution to the total EEL spectrum from one atom with (c) and without (d) a core-hole

be to explore the possibility of creating supercells, or in some way reducing the symmetry of the unit cell so that equivalent atoms are further apart. It may be that this is easier for one of the C_{60} structures and that might be the way to continue in order to compare a full core-hole simulation (a sum of the core-hole simulations carried out for each of the inequivalent atom) to a non core-hole calculation to gauge the effect of the core-hole.

This core-hole has been included by exciting a full electron from the core-state. If a full core-hole calculation was carried out, it might be found that this is not a good core-hole approximation for this structures, and that the

core-hole needs to be included in a different way, for example by only exciting half an electron.

7.2 Modelling spectra from endohedral fullerenes

The work presented here on pristine fullerenes C_{60} and C_{70} demonstrates how powerful the combination of experiment and theory can be in the understanding of materials. This combination is particularly important as monochromated TEMs become more common, as the extra information obtained from the fine-structure can often only be understood by comparison to simulated spectra.

One of the natural ways for this work to continue would be with the modelling of EEL spectra from endohedral fullerenes. Combining experimental data, including accurate experiments to determine onset energies, with simulated spectra could provide information about the electronic structure of these materials, including charge transfer between the cage and encapsulated atoms. It would also be interesting to see if any effect was observed on the electronic structure of endohedral fullerenes due to changes in bond lengths.

The experimental work carried out here has focused mainly on the carbon K-edge. Another useful extension to this work would be a more careful consideration of the encapsulated atom edges. This may be difficult because of the decreasing signal at larger energy losses and the larger amount of intrinsic broadening in some of these edges, although this broadening may mean that the energy resolution is not as important. Longer exposure times,

although increasing the SNR of an edge, also result in a greater amount of damage to the sample. Low temperature experiments may be useful for reducing the damage once the difficulty of substances condensing onto the sample has been overcome.

As well as using simulations to interpret experimental data, they could also be used to help plan experiments. Endohedral fullerenes are expensive to produce, and often there is only a very small amount of material. Although EELS does not need a great deal of material, spectra from similar materials could first be simulated in order to find out if the experiments are likely to show any differences. For these simulations to be reliable, a greater understanding of the core-hole effects, discussed in the previous section, in fullerene based materials needs to be achieved.

7.3 Spatial resolution

Nanotubes filled with fullerenes have been investigated by using spatially resolved EELS by Suenaga *et al.* [19]. This type of material would be a good extension for the techniques used in this investigation after they had been successfully applied to endohedral fullerenes. Modelling of these systems would be difficult for WIEN2k, but perhaps other codes, such as the FEFF 8 code mentioned in Chapter 3, could be used.

Another difficulty involved in obtained spatially resolved EEL spectra is the use of a small probe, and the damage that this can cause. Short exposure times would need to be used, and this may cause problems in obtaining a good signal from edges at relatively high energy losses.

7.4 Energy resolution

The work in this thesis demonstrates that high energy resolution is needed to see differences in the spectra from similar fullerenes. Exactly how high the resolution needs to be in order to tell the difference between two specific materials is difficult to estimate. Simulations should be able to help in this, but the work in Appendix B on the broadening of EEL spectra would need to be extended so that parameters in the simulation can be related more easily to the parameters in the experiment; for example the same instrumental broadening factor produces different results in the TELNES and TELNES2 codes.

7.5 Contamination

The experimental work carried out in this thesis has highlighted the need for the elimination of any unknown substance on or in the sample. This is particularly important as monochromation allows more details in the fine-structure to be seen, and these details can only be interpreted correctly if they are coming from the sample rather than from contamination. In order to continue with low temperature experiments, more information would need to be obtained on the nature and source of the low temperature contaminant so that it could be eliminated. This could perhaps involve looking at the spectrum from plasma cleaned grids, and seeing if other instruments suffer from the same problem.

The C K-edge has been found to be very sensitive to contaminants. This

sensitivity of fine structure could provide a very powerful tool. It may be that it is possible to attribute the strong features that have been observed to particular bonding environments and that this could be used to analyse other materials. On the other hand, it may be that this is impossible, and that the peaks can never be unambiguously identified due to the similarity of spectra from different environments. Perhaps only in parallel with other techniques will all the information available in the fine-structure be extracted.