Appendix A

Experimental techniques for investigating electronic structure

Several experimental techniques used to probe electronic structure are referred to in this thesis. In this section, some of these techniques and the information that they provide about electronic structure are outlined.

Electron Energy Loss Spectroscopy (EELS) EELS uses an electron beam to excite the electrons in a sample. By measuring the amount of energy lost by the electrons in the beam, it is possible to probe the unoccupied states and phonon energies. It is possible to obtain information on the bonding and environment of different elements as well as the optical properties.

Electron Spin Resonance (ESR) ESR measurements determine whether a molecule has an unpaired electron in it by using a phenomenon known as electron spin resonance. An unpaired electron has two possible spin states in a magnetic field which correspond to two energy values. If an incident

photon has an amount of energy corresponding to the difference in energy between the two levels, it can be absorbed by the electron allowing it to flip from one spin state to the other.

Inverse Photoemission Spectroscopy (IPES) In IPES the sample is exposed to a beam of electrons. Some of these electrons will undergo transitions into the empty states above the Fermi level emitting a photon. By knowing the original beam energy and measuring the energy of the photon emitted, it is possible to use IPES to probe these unoccupied states. This technique is not element selective [11] and spectrum from individual elements overlap.

Photoemission spectroscopy (PES) PES involves the excitation of an electron from a state below the Fermi level using UV light (UPS) or x-rays (XPS). The kinetic energy of the photoelectron gives information about the binding energy of the state from which the electron came. It probes the density of states below the Fermi level. As the released electrons has a mean free path of a few nanometres and needs to escape from the sample in order to be recorded, this technique is surface sensitive [12]. A combination of PES and IPES can be used to determine the band gap of a material.

UV-Vis-NIR absorption spectroscopy In UV-Vis-NIR spectroscopy photons with wavelengths from the ultra violet to nearly infra red are used to obtain an absorption spectrum from a sample. This spectrum is affected by the structure of the molecule.

X-ray absorption spectroscopy (XAS) When an x-ray travels through a material, a proportion of the beam is absorbed which is a function of energy. Superimposed on this smooth variation is a series of absorption edges which correspond to the ejection of a core electron and these edges are characteristic of each element. The core electron is excited to a state above the Fermi level and so this technique probes the unoccupied density of states. Changing the x-ray energy changes the unoccupied density of states that the electron can reach. The excited states decay by fluorescence or Auger decay and it is the decay process that is recorded. The edge comprises a jump preceded and followed by a series of oscillations. Information on both oxidation state and coordination number can be obtained from the oscillations close to the edge [13]. The technique produces similar information to EELS, but is unable to obtain this information from a small area of the sample due to the difficulties involved in focussing the incident beam of x-rays.

X-ray emission spectroscopy (XES) In XES electrons or x-rays are used to remove core electrons from the sample. An electron in an occupied valence band will then move down to the core level, emitting an x-ray. This technique probes the density of states of the conduction or valence band, i.e. the band which the electrons move down from.

Appendix B

Broadening

In this chapter, the various sources of broadening of the EEL spectrum are discussed. Lifetime broadening is included in the simulation of EEL spectra from the F1 and C1 structures that were discussed in Chapter 4. The effects of varying some of the broadening parameters on those spectra are also discussed.

B.1 Sources of broadening

All the simulated EEL spectra that have been presented in the previous chapters have been calculated using the TELNES program, which is part of the WIEN2k package. This program includes only an instrumental broadening factor in the simulation of the EEL spectra. In reality there are three sources of broadening [14, 160]:

- Instrumental broadening
- Core-state broadening
- Final-state broadening

Instrumentation broadening is a combination of the resolution of the spectrometer and the energy spread of the electron beam, as discussed in Chapter 2. The finite lifetimes of the core state and the final state result in an uncertainty in the energy of the states. The width in the energy of the core state, Γ_i, is given approximately by the uncertainty relation

$$\Gamma_i \tau_i \approx \hbar \tag{B.1}$$

where τ_i is the lifetime of the core-hole, which depends on the deexcitation mechanism. This means that Γ_i depends mainly on the excitation energy of the edge [14]. There is a similar broadening due to the lifetime of the final state. If τ_f is expressed as λ/ν, where λ and ν are the wavelength and the velocity of the ejected core electron respectively, then

$$\Gamma_f \approx \frac{\hbar \nu}{\lambda} \tag{B.2}$$

It has been found that λ is inversely proportional to the kinetic energy (E_{kin}) of the ejected electron for E_{kin} less than 50 eV [14]. If a free-electron approximation is used, $\nu = (2E_{kin}/m_0)^{\frac{1}{2}}$. This means that Γ_f is proportional to $E_{kin}^{\frac{3}{2}}$, and it will increase with distance above the edge onset. The most difficult source of broadening to account for is that due to the lifetime of the final state.

B.2 Simulation of spectra with energy dependent broadening

The TELNES2 program in the WIEN2k package includes all three sources of broadening. The instrumental broadening is included as a Gaussian function, the width of which is specified in the input file. The core-state lifetime broadening is included as a Lorentzian function which is element specific and taken from a table of data. The final state lifetime is included using a Lorentzian function. As the width is unknown, there are three approximations which it is possible to use:

- Γ_f is a constant
- Γ_f is given by a function linearly dependent on the distance from the edge onset
- Γ_f is given by a quadratic function

The approximation Γ_f equals a constant is that which is used in the TELNES program already used to simulate EEL spectra. The effects of a linearly dependent broadening factor on the EEL spectra calculated using the TELNES2 package from the C_{60} structures used in Chapter 4 can be seen in Figures B.1-B.4.

Figure B.1 shows the effect of varying the instrumentation broadening on spectra simulated from the F1 unit cell. The spectra also include a linear energy dependent broadening term which varies as E/γ where E is the energy above the edge onset and γ is a number (10 is used here which is the

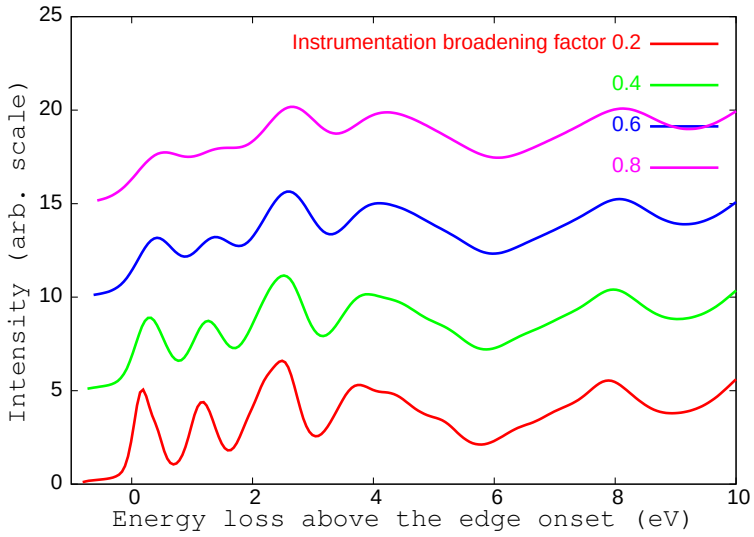

Figure B.1: The effect of instrumentation broadening on simulated spectra from the F1 unit cell

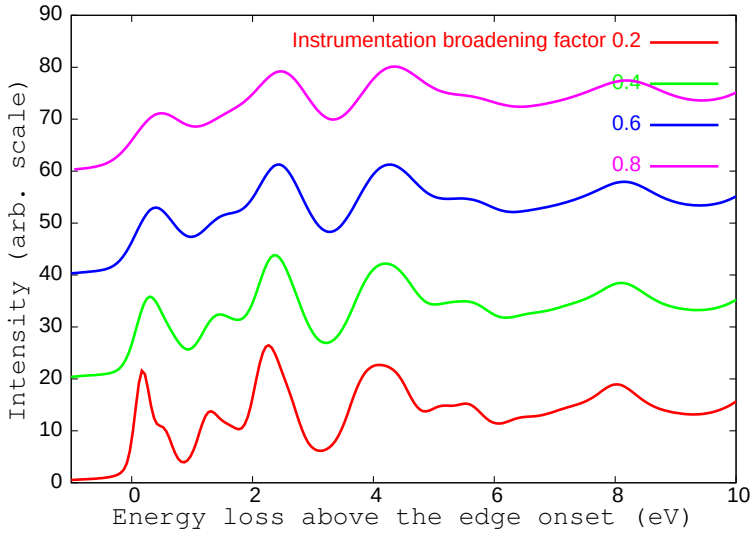

Figure B.2: The effect of instrumentation broadening on simulated spectra from the C1 unit cell

default). This is repeated in Figure B.2 for the C1 unit cell. From these two figures, it can be seen that the instrumentation broadening affects the sharpness and intensity of the peaks. When the value of the instrumentation

broadening reaches about 0.6 eV, it is becoming difficult to tell the difference between the spectra from the two samples. It is worth noting that the input for the TELNES and TELNES2 programs are slightly different so that an instrumentation broadening value of X for the TELNES2 program does not correspond to a broadening factor of X in the TELNES program.

The added effect of the energy dependent broadening allows us to look more closely at the part of the spectrum with energy losses greater than 4 eV above the onset energy. The fourth peak, at around 4 eV above the edge onset is seen to shift between the two C_{60} crystal structures. It appears at 3.8 eV in the F1 case and 4.1 eV in the C1 case. The position of this peak above the edge onset in the experimental data shown in Chapter 5 was at 4.3 eV for the nanocrystalline case and about 4.0 eV for the thin film case.

In Figures B.1 and B.2, the energy dependent broadening is included using an $E/10$ function. The default value of 10 was chosen as a rough fit to some lifetimes determined by experiment [161]. The effect of changing γ for a fixed instrumentation broadening of 0.4 eV is shown in Figure B.3 for the F1 unit cell and Figure B.4 for the C1 unit cell.

It can be seen from Figures B.3 and B.4 that γ effects how close to the edge onset details in the spectrum are smeared out. In the case of the spectrum from the C1 unit cell, this effects how distinct the second and third peaks are. A combination of changing the instrumental broadening and γ could lead to the second and third peaks in the spectrum merging, and producing a single broad peak. The amount of broadening needed to do this is not necessarily the same as the amount of broadening present in the experimental data, and

care needs to be taken when including broadening in simulated spectra.

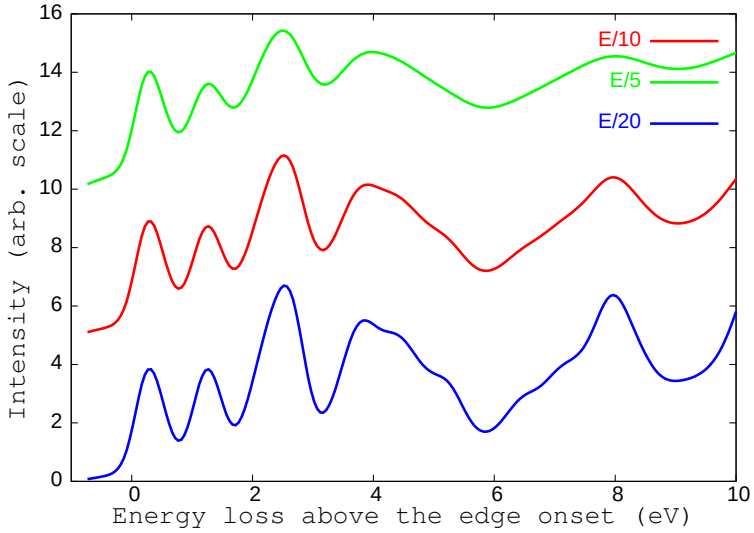

Figure B.3: The effect of changing γ on simulated spectra from the F1 unit cell

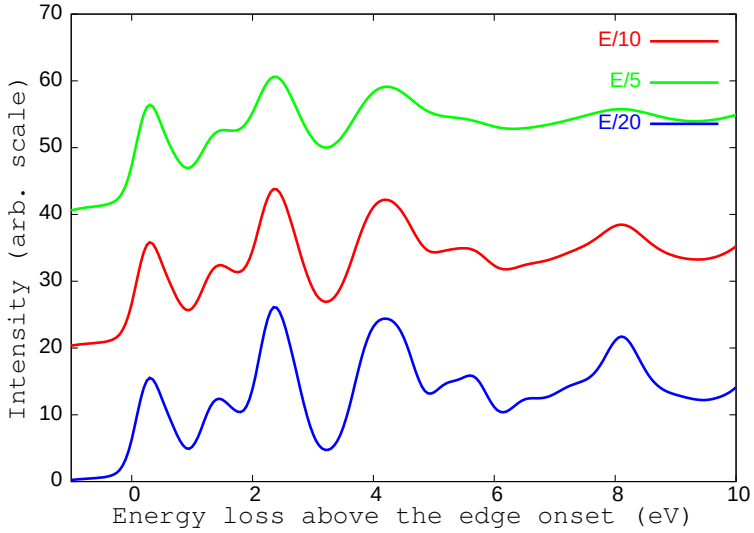

Figure B.4: The effect of changing γ on simulated spectra from the C1 unit cell

B.3 Summary

- Spectra have been simulated using different broadening factors: Spectra have been simulated with varying broadening factors, and it has been found that the broadening influences the amount of detail seen in the spectrum. Care needs to be taken when applying the broadening as it can have a dramatic effect.

Appendix C

Vienna Ab-initio Simulation Package

The Vienna Ab-initio Simulation Package (VASP) is a DFT package which is designed to carry out molecular dynamics (MD) simulations. The ground state electronic configuration is calculated at each MD step and then force and stress tensors can be calculated and used to relax the atoms. Pseudopotentials, or the projector-augmented wave (PAW) method can be used to describe the interaction between the ions and the electrons and a plane wave basis set is used.

Using the pseudopotentials or PAW method means that the number of plane waves needed in the basis set can be kept small. This makes the calculation of the ground state much faster than codes such as WIEN2k, and MD simulations are feasible.

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