Modelling paramagnetism in EELS: a study of magnetic order

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Abstract. Magnetic ordering has been shown to have a significant effect on the shape of the oxygen K-edge energy-loss near edge structure (ELNES) in a series of chromite spinels. However, the ELNES of these materials has only been simulated using a rough approximation of antiferromagnetism - the true nature of the magnetic interactions responsible for the detailed oxygen K-edge shape is still unknown. Chromite spinels typically undergo transitions to long range ordered antiferromagnetic (AFM) structures at temperatures below ~15K. Dynamic short range magnetic order (SRO) has been observed at temperatures up to 150K using neutron powder diffraction (NPD). It is not clear whether long range magnetic order, short range magnetic order or paramagnetic effects are responsible for the characteristic oxygen K-edge ELNES observed at room temperature. Here we discuss the possibility of carrying out paramagnetic simulations using the real space multiple scattering program FEFF8.2, and show preliminary results of paramagnetic simulations of the oxygen K-edge ELNES of magnesium chromite.

1. Introduction

Electron energy-loss spectroscopy (EELS) carried out in the scanning transmission electron microscope (STEM) can be used to probe the structure, bonding and electronic structure of a material with close to atomic scale spatial resolution [1]. Ionisation edges occur when the electron beam causes the core electrons of the atoms in a sample to be excited into unoccupied energy levels. The energy-loss region up to ~40 eV above this edge onset is termed the energy loss near edge structure (ELNES) and is closely related to the band structure or local density of states of the material. Interpreting ELNES to obtain information on the bonding and structure of complex materials is a relatively recent concept, and one which is not yet fully understood. Supporting systematic experimental studies with theoretical simulations can give new insights into the mechanisms responsible for the characteristic ELNES of ionisation edges.

An experimental study of the oxygen K-edge ELNES of chromite and ferrite spinels [2] generated spectra which could not be simulated accurately using conventional calculations [3]. Chromite and ferrite spinels (AB²O₄ where A = divalent cation and B = Cr, Fe) typically undergo transitions from paramagnetic states to long range AFM states at temperatures below 20K. Normal spinels experience geometric magnetic frustration from the tetrahedral arrangement of the B-site cations, and in many cases, the true magnetic structures of such materials are still unknown.

Calculations using the local spin density approximation (LSDA) within density functional theory (DFT) [4] have shown that including antiferromagnetic order in the simulation of the oxygen K-edge
ELNES of magnesium chromite significantly improves the agreement between theory and experiment, despite the fact that the experimental data was collected in the electron microscope at ambient temperature. Neutron powder diffraction measurements have detected dynamic short range magnetic order (SRO) in zinc ferrite [5], magnesium chromite and zinc chromite [6] at temperatures up to ten times the Néel temperature, $T_N$.

A series of magnetic simulations are required to identify the interactions responsible for the characteristic oxygen K-edge ELNES exhibited by these systems. In particular, long range AFM order, short range magnetic interactions, and paramagnetic effects must all be modelled. In this paper we discuss the difficulties of paramagnetic simulations, and propose a method which may be used to approximate paramagnetic interactions.

2. Paramagnetic Simulations

A true paramagnetic simulation is not possible using the simulation methods available at present. A calculation in which all crystallographically equivalent chromium or iron atoms in the crystal structure must contain independent, randomized magnetic moments in the basis set would be extremely computationally expensive. Additionally, almost all generally available simulation programs require a collinear spin arrangement. A version of the WIEN2k code capable of performing non-collinear spin polarised calculations has recently been released [7], but has only been used in the calculation of correlated spin systems such as spin spirals, and requires extensive computational resources. A true paramagnetic calculation would include no correlation between spins, significantly increasing the computational resources required.

An approximation to a paramagnetic calculation may be made by calculating as many differently ordered spin configurations as possible, and summing all spectra to obtain a weighted average spectrum. This method will unavoidably include a treatment of spin correlation, and is restricted to just two relative spin orientations (spin-up and spin-down). The conventional unit cell of a cubic, fully normal spinel contains 16 B-site cations, which corresponds to $2^{16}$ (65,536) possible collinear spin arrangements. Further simplification is required to make the calculation viable. The approximate paramagnetic simulation shown here includes spectra calculated using every possible spin arrangement in two octants of B-site cations in the convention unit cell (shown in figure 1 in a simple AFM spin alignment).

![Fig. 1 – Schematic of two octants in the spinel unit cell, showing the positions and spin orientations of the B-site cations in an antiferromagnetic alignment.](image)

There are five different ratios of spin up to spin down atoms available using this atomic basis set, shown in table 1 with their respective weightings (i.e. number of possible occurrences). The opposite spin ratios (e.g. 0 spin-up atoms to 8 spin-down atoms) are also calculated and summed with their respective ‘partner’. The oxygen K-edge ELNES for each given spin ratio has been calculated, and the results averaged using the weightings shown.
3. Experimental and Simulation Methods

Details of the experimental data collection have been published previously [3]. Briefly, the magnesium chromite spectrum was collected on a VG microscopes HB5 cold field emission gun (FEG) scanning transmission electron microscope (STEM) operating at 100kV. A Gatan 666 parallel electron energy-loss spectrometer controlled by Gatan EL/P software was used with a collection half-angle of 12 mrad. The full width at half maximum (FWHM) of the zero-loss peak was between 0.5 and 0.6 eV.

Calculations were performed using the simulation code FEFF8.2 [8]. This program simulates ELNES using a real space multiple scattering approach, wherein the electron excitation event is equivalent to an outgoing partial wave being characteristically scattered by the neighboring atoms in a surrounding cluster. By considering each coordination shell as an array of muffin-tin potentials, the interference effects on the scattered wave can be calculated. A series of calculations, in which the number of coordination shells considered is systematically increased, can give an insight into important scattering events.

The lack of symmetry constraints within the real space approach make this code ideally suited to a study of magnetism. Calculations have been performed using clusters of ~150 atoms, with a full core hole. FEFF8.2 includes a treatment of final state lifetime broadening, and no additional experimental broadening has been added. The AFM spectrum shown was calculated using the spin arrangement shown in figure 1.

4. Results and Discussion

Figure 2 shows the experimental oxygen K-edge ELNES of magnesium chromite, and the results of a series of FEFF8.2 ELNES simulations. In all FEFF8.2 simulations shown here, the fine structure (allocated to states created by the hybridisation of oxygen 2p and chromium 3d orbitals) was found to be compressed into a smaller energy range than in experiment. This may due to an inaccurate calculation of atomic potentials within the FEFF8.2 code.

The non-magnetic simulation (fig. 2a) shows fine structure in the K-edge which is not observed in the experimental data (fig. 2f). While the FM simulation (fig. 2b) appears to reproduce peaks A and B satisfactorily, an additional peak is observed between peaks C and D (marked *) which is not observed in experiment, and peak D is not accurately modelled. In the AFM simulation (fig. 2c), peak B is observed as a shoulder of peak A rather than as a discrete peak, and is significantly higher in intensity than in experiment, as is peak C.

The approximate paramagnetic simulation (fig. 2d) yields a spectrum extremely similar to the AFM case, although peaks B and C have a reduced intensity which improves the fit to experiment. This similarity is due to the fact that the paramagnetic spectrum is a weighted average of all possible spin orientations of 8 chromium atoms. This average is heavily weighted towards the more AFM-like spin ratios since there are many more possible configurations of these than any other type. Furthermore, the restriction of using collinear spin arrangements means that a high degree of correlation remains prevalent in the paramagnetic spectrum.

| No. of spin-up atoms | No. of spin-down atoms | Weighting |
|----------------------|------------------------|-----------|
| 8                    | 0                      | 1         |
| 7                    | 1                      | 8         |
| 6                    | 2                      | 28        |
| 5                    | 3                      | 56        |
| 4                    | 4                      | 35        |

Table 1 – The ratios of spin-up to spin-down atoms possible in the two octants of the spinel unit cell shown in figure 1, with their respective weightings.
5. Conclusions
The paramagnetic calculation presented above showed only a small improvement in the fit to experiment over the simpler AFM case. However, as noted, this calculation could only consider a broad approximation of paramagnetism. A full paramagnetic simulation requires a non-collinear spin treatment, and a true randomization of spin orientations. Further investigations must also focus on the simulation of the short range magnetic order reported to be present in these materials at temperatures well above $T_N$.

The discrepancies evident between the FM and AFM simulations presented above imply that EELS may also be sensitive to magnetic ordering type. Transitions between magnetic or ferroelectric states in materials are usually accompanied by a significant perturbation in the density of states. This perturbation should be detectable in ELNES spectra. The identification of a material which exhibits separate, characteristic ELNES spectra in different magnetic ordering regimes remains an important objective, which would emphasise the value of ELNES as a characterisation tool in magnetic systems.

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