ELNES as a probe of magnetic order in mixed oxides

D A Eustace\(^1\), F T Docherty\(^1\), D W McComb\(^2\) and A J Craven\(^1\)

\(^1\)Dept. of Physics and Astronomy, University of Glasgow, Glasgow, G12 8QQ
\(^2\)Dept. of Materials, Imperial College London, London, SW7 2AZ

Email: d.eustace@physics.gla.ac.uk

Abstract. A previous study of chromite and ferrite spinels revealed energy-loss near-edge structure (ELNES) in the oxygen K-edge that could not be reproduced in non-spin polarised calculations. Chromite and ferrite spinels typically undergo transitions to long range ordered magnetic structures at temperatures below \(-15K\). A model in which dynamic magnetic short range order (SRO) persists above the Néel temperature until 100K has been proposed using neutron powder diffraction. In the TEM, the interaction time of the fast electron with the specimen is sufficiently short for dynamic magnetic interactions to influence the observed ELNES at 300K. Here we present new spin polarised calculations performed using the commercially available codes FEFF8.2 and Wien97. The calculated oxygen K-edge ELNES show improved agreement with experiment when magnetic interactions are included in the calculation.

1. Introduction

Electron energy loss spectroscopy (EELS) carried out in the transmission electron microscope (TEM) can be used to probe the structure, bonding and electronic structure of a material with close to atomic scale spatial resolution. Ionisation edges occur when the electron beam causes 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 is termed the energy-loss near-edge structure (ELNES) and is closely related to the local density of states (DOS) of the material. By combining a systematic materials investigation with theoretical simulations, we can gain an insight into the processes contributing to ELNES shape and position.

A systematic investigation of chromite and ferrite spinels\(^3\) (ACr\(_2\)O\(_4\)/AFe\(_2\)O\(_4\) where \(A = \text{Mg}, \text{Zn}, \text{Co}\)) revealed fine structure in the oxygen K-edge ELNES which could not be reproduced using non-spin polarised calculations. Chromite and ferrite spinels are known to have ordered magnetic structures at low temperatures. Such spinels are magnetically frustrated systems due to the tetrahedral arrangement of the chromium and iron atoms, and this prevents a fully antiparallel arrangement of spins. The true magnetic structure of these materials is complicated and, in many cases, not yet fully understood. Neutron powder diffraction investigations by Schiessl et al.\(^4\) have detected dynamic short range magnetic order (SRO) up to ten times the Néel temperature, \(T_N\). Calculations using the local spin density approximation (LSDA) within density functional theory (DFT) have shown that including AFM order in the calculation of the oxygen K-edge ELNES of magnesium chromite\(^5\) improved the agreement between theory and experiment, despite the fact that experimental data was collected in the electron microscope at ambient temperature. A model in which dynamic SRO persists in chromite spinels to room temperature has been proposed. The short interaction time of the electron with the
sample, relative to that of the comparatively slow neutron, results in the dynamic SRO being detected to much higher temperatures in the TEM.

Here we present new spin polarised calculations performed on a range of chromium spinels carried out using two commercially available packages, FEFF8.2 and Wien97. The aim has been to reproduce results obtained by collaborators using a non-commercial code that makes use of the linear muffin-tin orbital (LMTO) theory within DFT. We also consider the effect of varying both the number of k-points and $Rk_{\text{max}}$ in Wien97 to minimize processing time without compromising data quality. $Rk_{\text{max}}$ is the muffin tin radius multiplied by the kinetic energy cutoff of the plane wave.

2. Experimental and calculation methods
Details of the chromite spinels investigated and the EELS acquisition parameters have been published previously. Calculations were performed using two commercially available computer packages, FEFF8.2 and Wien97. FEFF8.2 uses real space multiple scattering theory, wherein the electron excitation event is equivalent to an outgoing partial wave being scattered by neighboring atoms. By considering the surrounding coordination shells as an array of muffin-tin potentials, the interference effects on the scattered wave can be calculated. Such multiple scattering calculations do not require a periodic array of atoms, calculations were performed using cluster sizes of approximately 150 atoms.

A second approach is to consider that ELNES can be directly related to the local density of states after extraction of the necessary transition matrix elements. The formulation of local density of states is well established through various methods that make use of the LDA in DFT. Wien97 uses the Full Potential Linearized Augmented Plane Wave method within DFT to solve the Kohn-Sham equations for ground state electron density, total energy and energy bands of periodic solids in reciprocal space. Calculations are performed on a unit cell using a mesh of k-points in the Brillouin zone. The effects of varying the number of k-points and the $Rk_{\text{max}}$ value of the plane wave are presented here.

The excitation of an electron from an atomic core leaves a “core hole” which can have a significant impact on the shape of the density of states and consequently may influence the shape of the ELNES spectrum. In FEFF8.2, the effect of including a core hole may be easily investigated without increasing calculation time. Calculations shown here using FEFF8.2 include a core hole, but there is no significant difference if the core hole is not included. Including a core hole using Wien97 involves the formation of a supercell with lower symmetry and requires significant additional computing resources. Calculations shown here with Wien97 do not include a core hole.

FEFF8.2 automatically includes final state lifetime broadening in the calculation, the effect of which is to increase the amount of broadening applied to features as a function of the square of the energy above the edge onset, i.e. higher energy features are broadened more. Wien97 does not apply final state lifetime broadening. Both FEFF8.2 and Wien97 spectra may be uniformly broadened across all energies to account for limited instrumental resolution.

3. Results and discussion
In figure 1 the experimental oxygen K-edge ELNES of magnesium chromite and cobalt chromite, (a), are compared with the results from non-spin polarised calculations performed using Wien97 (d). The discrepancies between the experiment and theory are clear, and occur mostly in the energy region up to 10 eV beyond the edge onset. This part of the ELNES has been directly attributed to transitions to states created by the mixing of the chromium 3d and oxygen 2p orbitals. This region is most susceptible to changes in the chromium d-DOS that occur when magnetic ordering is considered.

Figures 1(b) and (c) show the results of spin polarised calculations of the oxygen K-edge ELNES of magnesium chromite and cobalt chromite performed using FEFF8.2 and Wien97 respectively. Magnesium chromite is antiferromagnetic (AFM) with $T_N \sim 14K$. Spin polarisation was included in the calculation using the same AFM spin configuration of chromium atoms as McComb et al. Cobalt chromite is ferromagnetic (FM) below its Curie temperature of 100K. In the calculations shown here the cobalt and chromium atoms were considered as having parallel spins.
Improved agreement with experiment can be seen in the magnesium chromite case. Considering the FEFF8.2 calculation, peak shapes A, B, C and D are similar to experiment. However, all peaks are narrower than in the experimental spectrum, and peaks B, C and D have shifted to lower energies. No instrumental broadening has been applied to this spectrum, as this results in the loss of peak B. Additional peaks are seen in the region immediately above peak D which are not observed in the experimental spectrum. The energy separation and width of peaks A-D is improved in the Wien97 calculation, although peaks B, C and D have shifted to lower energies. Peak D is incorrectly modelled, with additional shoulders observed which are not present in the experimental spectrum. 0.4eV instrumental broadening has been applied to this spectrum. Additional final state lifetime broadening is needed to ‘smooth’ the spectrum at higher energies, but this is not included in the calculation.

The ferromagnetic cobalt chromite calculation also shows an improvement in the fit to experiment. The errors in peak energy separation and width in the FEFF8.2 calculation are similar to the magnesium chromite case, but the main features of the experimental data are again successfully reproduced. In the Wien97 calculation, peak energy separation is improved. The splitting of peak C, which is dependant upon A cation type, is much more obvious in the FEFF8.2 calculation. Peak D is featureless in both calculations, while in the experimental data there is a clear shoulder on the lower energy side. Both calculations show a pre-peak, *, that is not present in the experimental spectrum. 0.4eV instrumental broadening has again been applied to the Wien97 calculation.

The results of the spin polarised calculations obtained with FEFF8.2 and Wien97 compare favourably with the results of previously published LMTO calculations of magnesium chromite. All three methods show a dramatic improvement in agreement with experiment over the equivalent non-spin polarised calculation. While the energy separation of peaks A-D is improved using LMTO, peak B is still seen to move to lower energies, becoming merged with peak A in a similar manner as shown here. Peak D, which is not well modelled here, appears more flattened and featureless than experiment when calculated using LMTO methods and final state lifetime broadening is applied.

Figures 2 and 3 show the effect of varying two of the input parameters to the Wien97 code, the number of k-points used (figure 2), and R_kmax (figure 3). 0.4eV instrumental broadening has been applied to all the calculated spectra. It can be seen that above 50 k-points, the number of k-points used in the reducible Brillouin zone does not have a significant impact on the shape of the ELNES spectra produced. Figure 3 shows that the plane wave cutoff value used also has no impact on the shape of the ELNES spectra produced. However, both of these parameters must be optimised if the user desires accurate total energy measurements or other quantifiable crystal properties. If only a comparative
investigation of ELNES shape is required, then computation time can be saved by using less stringent criteria, in this case 100 k-points and an $R_{k_{\text{max}}}$ value of 6.

![Figure 2](image1.png)  
**Fig. 2** – Effect of increasing number of k-points in Wien97 calculation of AFM magnesium chromite.

![Figure 3](image2.png)  
**Fig. 3** – Effect of increasing plane wave cutoff, $R_{k_{\text{max}}}$, in Wien97 calculation of AFM magnesium chromite.

### 4. Conclusions

A model in which dynamic SRO persists in chromite spinels to room temperature is supported by spin polarised calculations performed using FEFF8.2 and Wien97. These calculations, performed with both antiferromagnetic and ferromagnetic ordering, show an increase in agreement with experiment over non-spin polarised calculations performed with the same codes. The calculations presented here compare favourably with those calculated using a non-commercial LMTO-based code. There are some discrepancies between theoretical and experimental spectra which may be attributed either to computational limitations of the codes used, or to incorrect modelling of the complex spin orientations within these magnetically frustrated systems. Further work must be done to try and accurately model these spin structures to ensure the best fit to experimental data.

### References

[1] R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 2nd Edition, Plenum Press, New York, 1996.

[2] “ELNES Investigations of Spinels”, PhD Thesis, F. T. Docherty, Univ. of Glasgow, April 2001

[3] F.T. Docherty *et al*, Ultramicroscopy, (2001), 86, 273

[4] W Schiessel, W Potzel *et al*, Phys. Rev. B (1996) 53 9143

[5] D W McComb, *et al*, Phys. Rev. B (2003) 68 224420

[6] Ankudinov, A.L., *et al*, Phys. Rev. B, (1998), 58, 7565

[7] P. Blaha, *et al*, *WIEN97*, An FP-LAPW Package for Calculating Crystal Properties,(Karlheinz Schwarz, Techn. Universität Wien, Austria), 1999. ISBN 3-950103-0-4

[8] Hohenberg, P. and Kohn, W., Phys. Rev., (1964), 136, B864

[9] K. Schwarz, J. Solid State Chem., (2003), 176, 319

[10] Kohn, W. and Sham, L.J., Phys. Rev., (1965), 140, A1133

[11] A. Scott, R. Brydson *et al*, Phys. Rev. B (2001), 63, 245105

[12] Blasse, G. and Fast, J.F., Philips Res. Rep., (1962), 18, 393

[13] U. Lüders, *et al*, Mater. Sci. Eng., (2004) B109, 200

*The authors thank Dr. Andrew Scott of the University of Leeds for helpful discussions concerning Wien97.*