Cation site occupancy in spinel ferrites studied by X-ray magnetic circular dichroism: developing a method for mineralogists

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Abstract: X-ray magnetic circular dichroism (XMCD) is an element-, site- and symmetry-selective spectroscopic technique that has the potential to provide quantitative information on site occupancies in ferri- and ferro-magnetic minerals. XMCD spectra derived from the Fe $L_{2,3}$ absorption edge of a series of synthetic spinel ferrites and natural magnetite were collected using synchrotron radiation and a 0.6 Tesla 'flipper' magnet. These spectra were used to assess their potential value to mineralogical investigations. By comparison with theoretical spectra, the site occupancies of the cations have been calculated and compared to previous studies using other techniques. The spectra of the Co, Ni, Zn and Mg ferrite spinels show considerable variation, reflecting differences in site occupancies. Although the cation ratios derived from the XMCD spectra are broadly similar to previous work, there are significant differences especially in the amount of octahedral Fe^{2+} present. Incomplete inversion is recognised in all the spinels analysed and the affinity of Co, Ni and Mg for the octahedral site and Zn for the tetrahedral site is confirmed; the preference of Co over Ni for tetrahedral sites is also revealed. XMCD spectra proved relatively straightforward to analyse but further refinement of the quantitative calculations is needed and detailed comparison with the information derived from other methods, especially Mössbauer spectroscopy.

Key-words: XMCD, spinel, ferrite, Fe *L*-edge, structure.

Introduction

Soft spinel ferrites of the chemical formula $M^{2+}O.Fe_2O_3$ have, in general, a low coercivity, high permeability, high magnetic saturation and low conductivity. These properties make them ideal for use in frequency selective circuits, radio receiver antennae, microwave waveguides and other high-frequency devices. In nature, spinel ferrites are common constituents of igneous rocks, often in concentrations of economic importance and are the main contributors to rock magnetism. Complex chemistries and cationic distributions result in a range of electrical and magnetic properties that have motivated extensive mineralogical and technological investigations (see Smit & Wijn, 1959; Nell & Wood, 1989; Waychunas, 1991; Kuiper *et al.*, 1997; Rondinone *et al.*, 1999). The potential of the cation ordering to provide petrogenetic information (geothermometry, oxygen fugacities), especially on mafic igneous rocks, provides a special interest to those studying mantle petrogenesis. This paper introduces the potential application of the unique element- and site-specific properties of X-ray magnetic circular dichroism (XMCD) to mineralogical studies by applying this technique to the problem of Fe site distribution in synthetic spinel ferrites. Although XMCD is a

well-established technique there have been few applications to spinels (Sette *et al.*, 1990; Kuiper *et al.*, 1997; Pong *et al.*, 1997; Pellegrin *et al.*, 1999; van der Laan *et al.*, 1999). While the interpretation of the data requires a detailed comparison with calculated spectra, we show that such an analysis is rather straightforward.

Spinels

Spinels are a chemically diverse group of metal oxides with a face-centred cubic structure in which ¼ of the available tetrahedral sites and ½ of the octahedral sites are occupied, resulting in a basic formula of $A[IV]B_2[VI]O_4$ (Fig. 1). The cationic sites are usually occupied by di- or trivalent transition metals in the ratio $M^{2+}:M^{3+}$ of 1:2. In a *normal* spinel, such as $MgAl_2O_4$ (the mineral named 'spinel'), Al^{3+} occupies the octahedral sites and Mg^{2+} the tetrahedral sites. In an *inverse* spinel, such as magnetite, $Fe^{2+}(Fe^{3+})_2O_4$, Fe^{3+} is split between the octahedral and tetrahedral sites and Fe^{2+} occupies only the octahedral sites; a spinel with all the Me^{2+} in the octahedral site is said to have an inversion ratio of 1.0. In addition to Fe, Mg and Al, natural spinels contain divalent
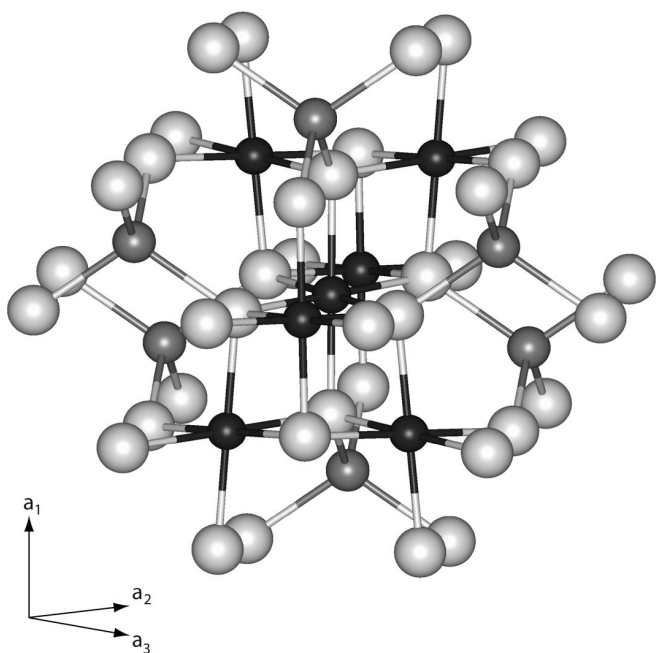
Fig. 1. The structure of a ferrite spinel showing the octahedral sites (small black spheres) and tetrahedral sites (small grey spheres). Oxygen is represented by large light grey spheres. (structure created using the programs Cerius^2 and Weblab Life, Molecular Simulations Inc.)

Fig. 2. Fe $L_{2,3}$ absorption spectra of $CoFe_2O_4$. The *L*-edge spectra were collected in a reversible 0.6 Tesla magnetic field (dashed and solid lines), and the resulting XMCD difference spectrum is shown below (intensity increased by a factor of three).

Ni, Co, and Zn, trivalent Cr, and V, and tetravalent Ti (see Hill *et al*, 1979; Waychunas, 1991 for reviews). Crystal field stabilsiation, oxidation state and ionic radii effects result in the preference of Ni^{2+}, Co^{2+}, Mg^{2+} and Fe^{2+} for the octahedral (B) site, while Zn^{2+} has a very strong affinity for the tetrahedral (A) site.

The site occupancies of cations in spinels have been studied by a variety of methods, the most extensively used being Mössbauer spectroscopy (see De Guire *et al.*, 1989; O'Neill, 1992; Na *et al.*, 1993; Lucchesi *et al.*, 1998), which provides information on the iron oxidation state and the degree of cation ordering as well as information on the magnetic structure. Neutron diffraction has also provided an insight into cation disorder in the $Fe_3O_4 - MgAl_2O_4$ series (Harrison & Putnis, 1998; Harrison *et al.*, 1999). Thermodynamic modelling using enthalpy-based disorder models has also been used to provide cation distribution and pseudopotential radii and has proved successful in showing inverse *versus* normal character of end-member spinels (Price *et al.*, 1982). Extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to study NiZn-ferrite films (Harris *et al.*, 1996) revealing the affinity of Zn for the tetrahedral site with Ni occurring in both tetrahedral and octahedral sites; anomalous X-ray scattering has been used to examine Co and Ni spinels (Waseda *et al.*, 1995).

XMCD and spinels

Magnetism and XMCD

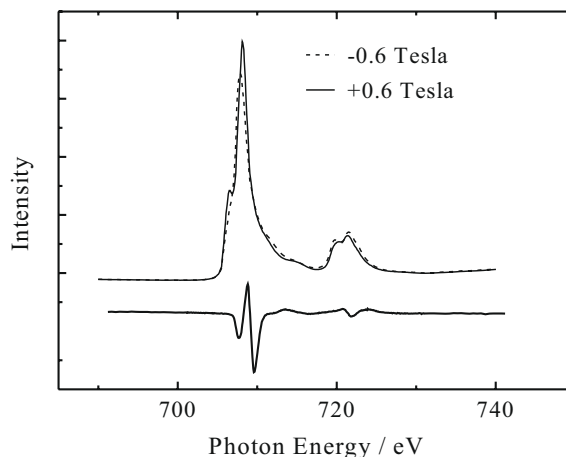The octahedral and tetrahedral sites in spinels form sub-lattices which can contain cations with opposite spins resulting in magnetisation which does not cancel out, hence resulting in ferrimagnetism. The magnetic moments of the tetrahedral cations (A sub-lattice) are anti-parallel to the octahedral ones (B sub-lattice). In an inverse spinel, such as magnetite, the anti-parallel Fe^{3+} spins on the octahedral and tetrahedral sites cancel out their magnetic contributions, and the ferromagnetic effect is provided by the M^{2+} in the B sub-lattice positions, as long as the metal concerned has unpaired electrons.

XMCD is the difference between the X-ray absorption spectra (XAS) of left and right circularly polarised X-rays. The absorption spectra of magnetic materials are collected in magnetic fields set parallel and anti-parallel to the helicity vector of the X-rays, which is along the beam direction. An example is shown in Fig. 2, which displays the Fe $L_{2,3}$ edge spectrum of $CoFe_2O_4$ collected by reversing the applied 0.6 Tesla magnetic field; the difference between the two absorption spectra provides the XMCD spectrum. At the $2p$ core levels of the $3d$ metals, where the electric-dipole transition excites the core electron into (partially) localised unoccupied states, XMCD provides information about the electronic and magnetic structure of the material. The technique has several advantages compared to its counterparts in the visible region, such as the magneto-optical Kerr effect and the Faraday effect. As the wave function of the involved core level is strongly localised and therefore well defined, XMCD is relatively straightforward to analyse, and, furthermore, the technique is element-, site- and symmetry-selective. Using synchrotron radiation, XMCD is a relatively uncomplicated technique, which has been used successfully to study a large variety of different systems such as rare earth and actinide metal alloys, thin films and multilayers. A major contribution to the success of this technique has been the development of a *sum rule* (Thole *et al.*, 1992) that states that the XMCD signal integrated over the $2p$ absorption edge is proportional to the orbital part of the $3d$ magnetic moment which has been qualitatively confirmed by band theory.
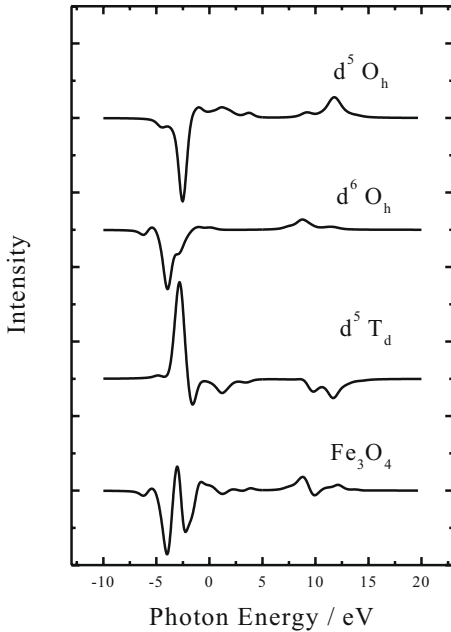
Fig. 3. The calculated Fe d^6 O_h, Fe d^5 T_d, Fe d^5 O_h components of the XMCD spectra of spinels (see text for details) and the theoretical resulting summed spectrum for Fe_3O_4.
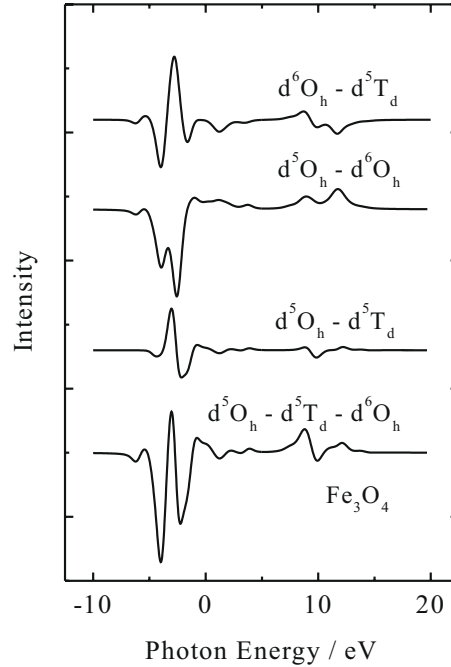

Fig. 4. The calculated binary mixtures of XMCD spectra. The spectra are constructed by summing two of the site occupancy components.

XMCD spectra

The $L_{2,3}$ absorption spectra for different polarisation directions can be calculated using the method described by van der Laan & Thole (1991) and from these the XMCD difference spectra can be derived. The XMCD spectrum of Fe_3O_4 comprises three main components which are derived from the three sites occupied by iron: Fe^{2+} octahedral (d^6 O_h), Fe^{3+} tetrahedral (d^5 T_d) and Fe^{3+} octahedral (d^5 O_h). The Fe^{2+} and Fe^{3+} ions at the octahedral (O_h) sites are aligned ferromagnetically and the Fe^{3+} ions at the tetrahedral (T_d) sites are coupled antiferromagnetically to those at the octahedral sites; in Fe_3O_4 the net moment due to the Fe^{2+} ions alone is ~4 μ_B per formulae unit.

The calculated spectra for the three individual components are shown in Fig. 3, along with an overall Fe_3O_4 spectrum, calculated from the sum of these components. The sign of the magnetic dichroism for each component is given by the direction of its magnetic moment. The relative energy positions of the calculated spectra for the different Fe sites were shifted to obtain the best fit compared to experimental spectra; adding them with a ratio of 1 : 1 : 1 gives a good agreement with previously reported magnetite films (Kuiper *et al.*, 1997). The chemical shift of roughly 2 eV between the spectra of the d^6 and d^5 ions is due to core-valence Coulomb interactions (van der Laan *et al.*, 1992). Small changes in the site occupancies can give a considerable difference in the relative peak intensities of the XMCD. Using these three components, it is possible to predict the spectral shapes of spinels with different ratios of $Fe^{2+/3+}$ (Fe d^6/Fe d^5) at the two sites (octahedral/tetrahedral – O_h/T_d) and 'binary' mixtures are shown in Fig. 4. A spinel ferrite with the formula $M^{2+}Fe_2O_4$ and an inversion ratio of 1.0 should contain Fe^{3+} in both octahedral and tetrahedral sites in a 1:1 ratio,
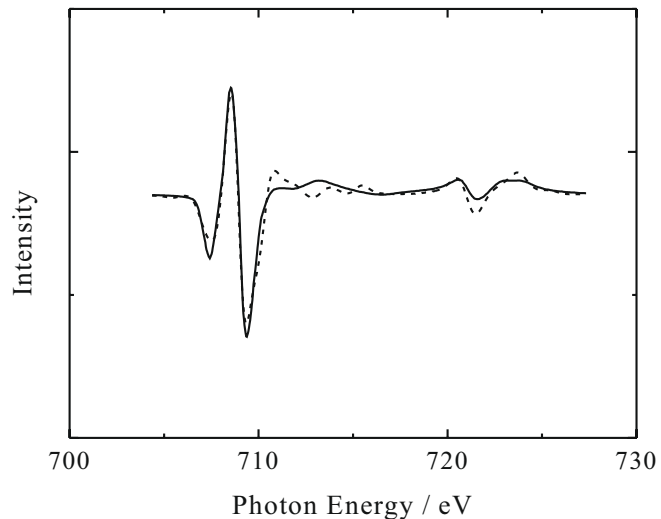

Fig. 5. The theoretical best fit (dashed line) for the experimentally derived XMCD $CoFe_2O_4$ spectrum (solid line) of the three theoretical site occupancy components (see Table 1).

while a normal spinel ferrite of the same formula should contain only Fe^{3+} in octahedral sites. Mixtures of the three theoretical components can, therefore, be fitted to experimentally derived spectra, producing site occupancy ratios of Fe at the three sites (see Fig. 5). In this study Fe^{2+} tetrahedral has been ignored – if it is included in the fitting process, a small component of < 0.1 atoms per unit formula may be present, but this is not thought to be statistically significant.

Calculation details

The $L_{2,3}$ spectra for the ground state and final states were calculated at $T = 0$ in intermediate coupling using Cowan's *ab initio* Hartree-Fock code with relativistic correction (Cowan, 1982). Interatomic screening and mixing were taken into account by reducing the *d-d* and *p-d* Slater integrals with scaling factors $k = 0.7$ and 0.8, respectively. For the octahedral sites a crystal field of 10Dq = 1.2 eV and an exchange field of $g\mu_B H = 0.01$ eV were used. For the tetrahedral site a crystal field of 10Dq = -0.6 eV and an exchange field of $g\mu_B H = -0.01$ eV were used. The calculated results were broadened by a Lorentzian of $\Gamma = 0.3$ (0.5) eV for the L_3 (L_2) edge to account for intrinsic linewidth broadening and a Gaussian function of $\sigma = 0.25$ eV for instrumental broadening. The main difference between these calculations and those presented by Kuiper *et al.* (1997) is a smaller crystal field at the octahedral sites, which leads to a slightly better agreement with the experimental results.

In principle, the local ground state at each site is a mixture of different configurations d^n and $d^{n+1}\underline{L}$, where the underscore denotes a hole on the oxygen ligand L (van der Laan *et al.*, 1986). The ground state depends on the *d-L* charge-transfer energy, the *d-d* Coulomb interactions, and the *d-L* mixing (hybridisation). The final state in XAS, where an electron has been excited from a 2*p* core level into an empty 3*d* state, is a mixture of the configurations $\underline{2p}3d^{n+1}$ and $\underline{2p}3d^{n+2}\underline{L}$. The hybridisation which mixes both configurations results effectively in a reduced multiplet width, which can also be interpreted as a reduction of the 2*p*-3*d* exchange interaction due to the delocalisation of the valence hole. Since the 2*p*-3*d* and 3*d*-3*d* Coulomb interactions are of similar size, the relative energy positions of the configurations in the initial and in the final state are also similar. Consequently, the change in hybridisation after 2*p* absorption will be small, which results in only a very weak charge-transfer satellite in XAS. Above the L_3 edge the calculation shows a low-intensity multiplet structure, which is broadened out in the experimental spectra. This indicates the presence of a charge transfer satellite. However, it is not meaningful to include the corresponding configuration in the calculation, since this would introduce additional parameters that cannot be determined properly. Therefore, we assume in the treatment of the spectra that each site can be represented by a single configuration with an integer *d* value. The reduction of the multiplet structure arising from the configuration mixing can simply be taken into account by scaling the Slater integrals. Such a single-configuration model offers a transparent analysis because the only parameters are the octahedral crystal field strength, 10Dq, and the scaling factors, *k*, of the Slater integrals.

Experimental methods

The samples used in this study were synthesised from stoichiometric mixtures of metal oxides (high purity Fe_2O_3, NiO, CoO, ZnO, MgO, Al_2O_3) held at 1100 °C for 3 days in air in a muffle furnace. All samples were reground after one day to help homogenise the reaction mixture and to speed up

Table 1. Site occupancy of iron in spinel ferrites calculated from the XMCD difference spectra. The spectra were fitted for three main spectral features derived from the Fe L_3 peaks only and ratios calculated to the number of Fe atoms per unit spinel formula.

Spinel composition	$d^6 O_h$	$d^5 T_d$	$d^5 O_h$	Cell parameter a, (Å) 1σ
Fe_3O_4, natural	0.90	0.90	1.20	8.3979(9)
$Co_{0.99}Fe_{2.01}$	0.13	0.84	1.03	8.3903(8)
$Ni_{0.99}Fe_{2.01}$	0.16	0.93	0.92	8.3381(7)
$Zn_{0.67}Fe_{2.33}$	0.51	0.54	1.28	8.4242(6)
$Mg_{0.85}Fe_{2.15}$	0.17	0.92	1.06	8.3887(4)
$Co_{0.52}Zn_{0.47}Fe_{2.01}$	0.16	0.70	1.17	8.4241(7)
$Ni_{0.48}Zn_{0.51}Fe_{2.01}$	0.16	0.81	1.12	8.3937(7)
$Co_{0.5}Mg_{0.47}Fe_{2.03}$	0.16	0.87	1.00	8.3880(13)
$Ni_{0.50}Mg_{0.50}Fe_{2.00}$	0.15	0.92	0.93	8.3636(4)
$Co_{0.44}Ni_{0.47}Fe_{2.09}$	0.15	0.89	1.05	8.3608(7)

the reaction. Some samples (Mg and Zn end-members) were crystallised at 1250 °C in an attempt to reduce some of the iron from ferric to ferrous. Sample purity was confirmed by X-ray powder diffraction and the room temperature cell parameters were determined using Si as an internal standard. The cell parameter a, derived from the spinel ferrites shows small variations with composition (Table 1). These are in line with those previously published which, for instance, reveal Zn-spinel ferrites to have the largest cell size and Ni-spinel ferrites the smallest (see Waychunas, 1991). Chemical compositions were derived using electron probe microanalysis employing a Cameca SX100 microprobe in the Williamson Research Centre, at the University of Manchester. Wavelength dispersive spectrometry at an operating voltage of 15 keV and a specimen current of 20 mA and pure metal standards were used. Oxygen was calculated by stoichiometry and the formulae in Table 1 assume $M^{2+} + M^{3+} =$ 3 atoms per spinel formula unit.

XMCD of the samples were measured using beamline 1.1 of the Synchrotron Radiation Source (SRS) at CLRC, Daresbury Laboratories. This beam line is equipped with a high-energy spherical grating monochromator providing 75% circularly polarised X-rays in the energy region of interest. The energy scale was calibrated using the Fe L_3 peak of Fe metal, assuming a photon energy of 707.7 eV for pure Fe (Chen *et al.*, 1995). The finely powdered samples were mounted on conducting tape on a copper plate placed between the coils of an electromagnet with soft-iron pole pieces used to generate fields up to ±0.6 T with switching times of 0.5 s, in a vacuum chamber (10^{-7} torr) (Dudzik *et al.*, 2000). The sample magnetisation was (anti)parallel to the direction of the X-ray beam. The dichroism spectrum was measured by switching the applied magnetic field for every energy point. Compared to energy sweeps with a fixed magnetic field, this eliminates the influence of beam drift and instability and it avoids errors due to backlash in the mechanical parts of the monochromator. The absorption signal was collected in total-electron yield mode and normalised to the incident X-ray flux. The XMCD spectrum was determined from the difference between the spectra collected for the two magnetisation directions (Fig. 2).
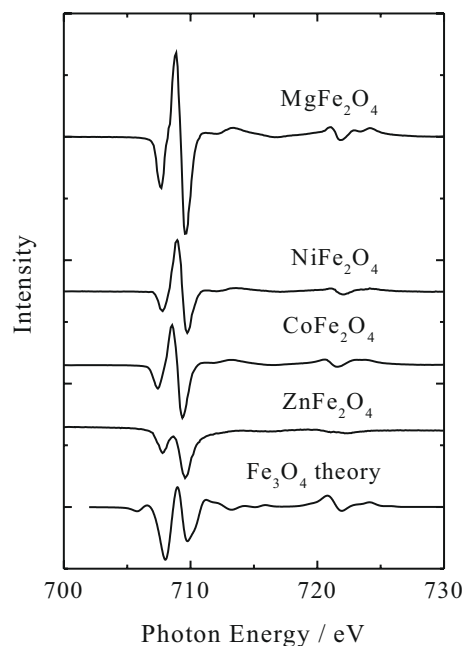
Fig. 6. The experimentally derived XMCD spectra of end-member Co, Ni, Zn and Mg spinel ferrites. The theoretical XMCD spectrum for Fe_3O_4 is also shown.

The site-occupancy ratios derived from the experimental spectra are shown in Table 1. Using the program CFIT, the best fit to the three theoretical components Fe $d^6 O_h$, Fe $d^5 T_d$ and Fe $d^5 O_h$ was determined for the part of the Fe L_3 XMCD spectrum covering the three main peaks between approximately 704 and 712 eV.

XMCD spectra of synthetic spinels and magnetite

End-member ferrites

The spectra derived from the end-member spinel ferrites are shown in Fig. 6. $CoFe_2O_4$ with an inversion ratio of 1.0 would only contain Fe $d^5 O_h$ and Fe $d^5 T_d$ but comparison between the theoretical spectrum of a 1:1 mixture (Fig. 4) and the experimental spectrum (Fig. 2 and 6) shows significant differences with slightly lower Fe $d^5 T_d$ and a significant Fe $d^6 O_h$ intensity (see also Kuiper *et al.*, 1997). A good fit is achieved with a ratio of 0.13 Fe $d^6 O_h$, 0.84 Fe $d^5 T_d$, 1.03 Fe $d^5 O_h$. This indicates that 84% of the Co is in the O_h site (giving an inversion ratio of 0.84) and the presence of Fe^{2+} causes a potential charge imbalance, unless Co^{3+} is present. Charge balance requires about 13% of the Co to be trivalent. Previous studies have also revealed evidence that $CoFe_2O_4$ formed at high temperatures and cooled quickly is not fully inverted and there is a correlation between a disordered distribution of Co and fast cooling rates. For instance, anomalous X-ray scattering indicated only 78% of the Co in a Co-Fe_2O_4 (prepared by synthesis at 1073 K) is in the octahedral site (Waseda *et al.*, 1995), which is consistent with the results of diffraction studies (O'Neill & Navrotsky, 1983).

Mössbauer spectroscopy indicated the presence of both Fe^{3+} T_d and a small component of $Fe^{2+} O_h$ leading to the suggestion that Co^{3+} is present in the tetrahedral sites (Na *et al.*, 1993; De Guire *et al.*, 1989).

The $NiFe_2O_4$ spectrum also shows three distinct peaks and a ratio of theoretical components of 0.16 Fe $d^6 O_h$, 0.93 Fe d^5 T_d, 0.92 Fe $d^5 O_h$. This distribution indicates there are 0.08 atoms Ni in the tetrahedral site, 0.91 atoms in the octahedral sites and, to maintain charge neutrality 0.16% of the nickel should be Ni^{3+}. In comparison with the Fe site occupancies in $CoFe_2O_4$, the Fe^{3+} is more evenly distributed, reflecting a relative preference of Co over Ni for tetrahedral sites; this is consistent with the crystal field stabilisation energies of Co^{2+} > Ni^{2+} in tetrahedral and Ni^{2+} > Co^{2+} in octahedral sites.

Two samples of Zn-Fe spinels were synthesised, with compositions of $ZnFe_2O_4$ and $Zn_{0.67}Fe_{2.33}O_4$, respectively. The first sample was non-magnetic and the latter weakly magnetic resulting in a weak XMCD spectrum. End-member $ZnFe_2O_4$ might be expected to be a strong ferrimagnet as the B site in $ZnFe_2O_4$ would be predominately occupied by Fe^{3+} and Zn^{2+} (d^{10}) has no cancelling magnetic moment. However, it has been observed that spinel ferrites with high concentrations of Zn have lower net moments due to antiferromagnetic B-B interactions 'flipping' the Fe^{3+} spin direction and a weakening of the A-B superexchange (O'Handley, 2000; Harris *et al.*, 1996). The $Zn_{0.67}Fe_{2.33}O_4$ spectrum, although of reduced intensity, shows a predominance of the two octahedral peaks; the best fit is 0.51 Fe $d^6 O_h$, 0.54 Fe d^5 T_d, 1.28 Fe $d^5 O_h$. The strong affinity of Zn^{2+} for the tetrahedral site has been demonstrated in earlier investigations of spinels and no detectable inversion was observed in neutron diffraction, muon spin rotation/relaxation and Mössbauer studies on slowly cooled $ZnFe_2O_4$ (Waseda *et al.*, 1995; Schiessl *et al.*, 1996). However, small amounts of inversion have been recorded by powder diffraction analysis of samples formed by fast cooling with a maximum of 0.19 inversion recorded in $ZnFe_2O_4$ cooled from 950 °C (O'Neill, 1992). The XMCD spectrum confirms the predominance of Zn in the tetrahedral site and also suggests a small amount of inversion (0.13 atoms Zn in the O_h site) although the quality of the spectrum does not justify detailed analysis.

The $Mg_{0.85}Fe_{2.15}O_4$ sample also displayed XMCD due to its deviation in chemistry from stoichiometric $MgFe_2O_4$. A best fit spectrum of 0.17 Fe $d^6 O_h$, 0.92 Fe $d^5 T_d$ and 1.06 Fe $d^5 O_h$ shows the affinity of Mg for the octahedral site although incomplete inversion is indicated and 0.08 Mg atoms per unit formula are in the tetrahedral site. There is an indication of a small charge imbalance and a need for electron donors, although in this case the deficiency may be within analytical error. A relationship between inversion ratio, and formation temperature and cooling history has been observed in Mg-ferrites and O'Neill *et al.* (1992) record an inversion ratio of 0.72 using powder diffraction and Mössbauer measurements for a stoichiometric sample synthesised at 1100 °C.

Magnetite

The XMCD spectrum of natural magnetite is presented in Fig. 7 and compared to the calculated spectrum of stoichio-
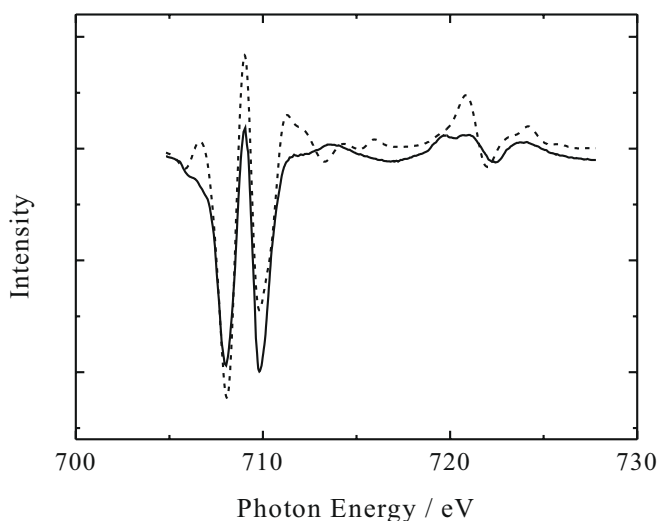
Fig. 7. Comparison of the experimentally derived natural magnetite spectrum (solid line) and the theoretical spectrum (dashed line) for Fe_3O_4.
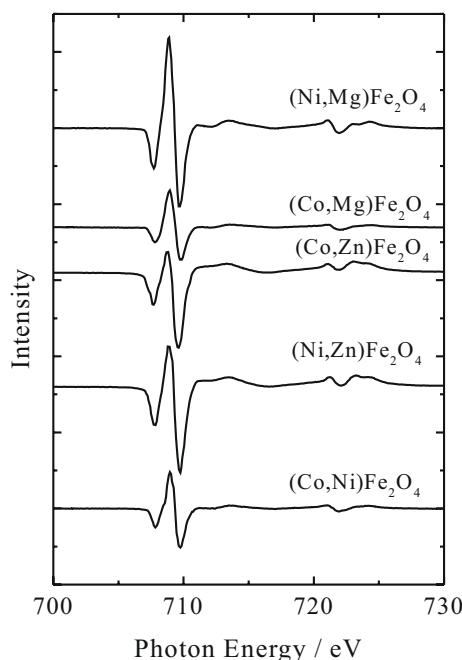

Fig. 8. The experimentally derived XMCD spectra of mixed cation (Co, Ni, Zn and Mg) spinel ferrites. The theoretical XMCD spectrum for Fe_3O_4 is also shown and the compositions of the spinel ferrites are shown in Table 1.

metric Fe_3O_4, and there are significant differences. Experimental spectra of synthetic thin films of Fe_3O_4 range from those similar to the theoretical spectrum (*e.g.* Kuiper *et al.*, 1997) to others similar to the natural sample analysed here (Schedin *et al.*, 2000). The main obvious difference is the lower intensity of the Fe d^5 T_d peak, which is particularly sensitive to any broadening of the spectral components; the spectra give a best fit of 0.90 Fe d^6 O_h, 0.90 Fe d^5 T_d and 1.20 Fe d^5 O_h. Chemical analysis of the magnetite revealed that it

contained minor amounts of other elements, namely 0.25 wt% MnO, 0.53 wt% SiO_2 and 0.25 wt% MgO, which are not enough to explain the variations in site occupancy ratios. This issue is further discussed below.

Mixed cation ferrites

The spectra of the spinel ferrites containing two M^{2+} are shown in Fig. 8 and the calculated ratios are given in Table 1. Compared to the spectra of the end-members $NiFe_2O_4$ and $CoFe_2O_4$, those of the Zn-containing samples, $(Zn,Ni)Fe_2O_4$ and $(Zn,Co)Fe_2O_4$, show an increase in Fe d^5 O_h and a decrease in the Fe d^5 T_d peak, relating to the Zn^{2+} substitution at the T_d site, which causes a reduction in the degree of inversion. However, it is also clear that a significant amount of the Zn must be at the T_d site, even if all Ni or Co is assumed to be octahedral. In comparison with the Fe site occupancies in $CoFe_2O_4$, Fe^{3+} is more evenly distributed and is further evidence of a relative preference of Co over Ni for tetrahedral sites; consistent with the crystal field stabilisation energies of Co^{2+} and Ni^{2+}. In contrast, the inclusion of Mg into Ni and Co ferrites has relatively little effect on the site occupancy ratios (Table 1) with a slight increase in the Fe d^5 T_d component due to Mg having more affinity to the octahedral site than Co.

Discussion

This study has revealed both the potential and the limitations of XMCD in mineralogical studies. It is clear that the XMCD spectra vary significantly with spinel composition and these differences can be quantified by fitting the three components of the theoretical spinel spectrum. Comparisons made (above) to previous work show that site occupancy ratios derived from XMCD are similar to those produced by other methods but with some significant differences. Variations in cation compositions and cooling history mean that direct comparison of data produced by the different techniques is only possible if conducted on the same samples.

Before the site occupancy ratios derived from XMCD can be accepted, several issues need to be clarified. Kuiper *et al.*, (1997) obtained a very good fit between the theoretical and experimental spectra of Fe_3O_4 in thin films. However, the failure of the theoretical fit of the bulk natural magnetite to produce a 1:1:1 ratio of site occupancy in the present study, clearly needs further investigation. During the present study other natural magnetite samples were analysed and produced varying degrees of resolution of the three main peaks in the XMCD spectra. This behaviour could not be related to trace element content. Furthermore, most of the spectra have a greater intensity at low energies than predicted, giving rise to a consistently higher amount of the Fe d^6 O_h than expected. Charge balance requires some of the Me^{2+} to be oxidised to Me^{3+}, which is plausible for Co but difficult to envisage for Ni and Mg. Kuiper *et al.* (1997) did notice that the theoretically derived positive peak at 707 eV was not present in the experimentally derived spectra of Fe_3O_4 from thin films, suggesting that low-lying thermally excited

states, where the $3d$ spin-orbit coupling is set to zero, may have to be considered in calculations.

However, a more fundamental explanation may cause these differences and this is the effect of the low energy of L-edge absorption. The use of total-electron yield means that this method is rather surface sensitive (at the Fe $L_{2,3}$ edge the mean electron escape depth is expected to be 17 ± 2 Å, (Nakajima *et al.*, 1999)), which means that effectively we measure only the top few atomic layers. Ideally, one would like to measure XAS in transmission mode but in the soft X-ray region, the specimen would have to be very thin in order to cope with the short absorption length of a few hundred Å. Also fluorescence detection is difficult due to the low fluorescence yield (~0.003), which leaves total-electron yield as the only viable option as the detection method in the soft X-ray energy region. This surface sensitivity could provide an explanation because the outer layer(s) in spinels might be different in stoichiometry due to the charge imbalance at the discontinuity caused by the surface; these atoms would contribute a significant proportion of the signal. Fundamental compositional differences in the surface region of magnetite are well known from detailed STM work (Lennie *et al.*, 1996) and for a surface such as (111) Fe_3O_4 there can be a number of different terminations exposing various combinations of tetrahedral and octahedral sites. However, it is impossible to envisage a consistent structural and compositional surface developed from a ground, powdered sample. Another possible explanation is the effect of redox or charge transfer processes at the surface region of samples in response to radiation used in the experiments; photoreduction can be a problem in XPS studies and electron hopping in magnetite is a well known phenomenon which results in no discrete Fe^{2+}/Fe^{3+} in octahedral sites above the Verwey transition.

It is also worth noting that the disagreement between theory and experiment for the spectral structure at photon energies higher above the onset (> 711 eV) is due to effects that have been neglected in the calculation. The theory does not include configurations that are higher in energy and their presence might, therefore, be responsible for the spectral differences in the range 710 to 715 eV. The spectral appearance of the L_2 edge can be changed by Coster-Kronig interaction between the discrete states $2p_{1/2}3d^n$ and continuum states $2p_{3/2}3d^{n-1}k$, where k is a continuum electron. As a result, although the calculation is reliable for the three peaks of interest in the L_3 region, the structure at higher energies is not suitable for quantitative analysis.

We need to understand these issues relating to the spectra before we can be confident of quantitative calculations of site occupancy. Although XMCD is much more surface sensitive than other techniques used for analysis of site occupancies in spinels, it is the only one able to obtain the element and site specific magnetic moments. Mössbauer spectroscopy has been the main method of analysis of iron in spinels and the systematic comparison of spectra derived by XMCD and Mössbauer spectroscopy should lead to this clearer understanding of the nature of the data provided by both methods. They may well prove to be complementary and we are currently undertaking such comparative studies. XMCD has another major advantage over techniques such as Mössbauer spectroscopy in that spectra can be collected for elements other than Fe, such as Ni, Co, Cr and Mn. These spectra can yield information on the valency and coordination of these other ions, complementary to the iron spectra, and such spectra are currently being collected for cobalt in a detailed study of the Co-Fe spinels.

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