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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

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