X-ray magnetic circular dichroism in cobalt-iron spinels and electronic states of Co ions

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Synchrotron X-ray experiments on magnetic circular dichroism (XMCD) have been performed at Co K and Fe K absorption edges for $CoFe_2O_4$, $Fe_{1.5}Co_{1.5}O_4$ and $FeCo_2O_4$ with the spinel structure. The XANES studies have clarified that only Fe^{3+} exists in all compounds and Co^{2+} and Co^{3+} coexist in the latter two cobaltites. A systematic change in XMCD spectra has concluded that the Co^{2+} ions in the B sites of $FeCo_2O_4$ are in the low-spin state. Since the Co^{2+} ions in $CoFe_2O_4$ are in the high-spin state, the spectra of the intermediate cobaltite may be explained as a mixture of low-spin and high-spin states.

Keywords: X-ray magnetic circular dichroism, XMCD, cobalt ferrite, cobaltite, electronic state.

1. Introduction

With well-defined polarized synchrotron X-rays, X-ray magnetic circular dichroism (XMCD) experiment becomes a useful tool for studying ferrimagnetic materials to extract precise quantitative information on atomic magnetic moments.

In ferrites, Fe^{3+} ions having a large spin polarization give strong magnetic moments through the super exchange interaction between the tetrahedral A and octahedral B sites. Replacing Fe^{3+} by the other transition-metal ions, the ferrimagnetic property weakens or disappears. Cobalt ions are a notable example to be ferrimagnetic at room temperature except Fe^{3+}. Cobalt-iron oxides $Co_xFe_{3-x}O_4$ are ferrimagnetic materials with the spinel structure, in which the cations are distributed over A and B sites. The cation distribution for the end-members is almost inverse-type, where the majority of Co^{2+} is located at the B sites with the Fe^{3+}. The effects of the substitution of Co^{3+} are interested in the occupancy of Co^{2+} in the A sites and the Co^{2+}-Co^{3+} charge transfer. Mössbauer spectroscopy shows that Co^{3+} is located at the B sites and Co^{2+} moves from the B sites to A sites when the substitution of Co^{3+} occurs (Smith *et al*., 1978; Martens *et al*., 1985).

The magnetic structure of $Co_xFe_{3-x}O_4$ ferrite has been deduced from magnetization anisotropy (Slonczewski, 1958), saturation magnetization measurements (Takahashi and Fine, 1972) and neutron diffraction experiments (Teillet *et al*., 1993). Experimental works on XMCD for $CoFe_2O_4$ spinel have been reported at the Fe K-edge (Kawamura *et al*., 1997; Matsumoto *et al*., 2000). No XMCD data have been reported for cobaltite. Therefore, in this study, the difference in the electronic states between ferrite and cobaltite is examined by XMCD. By using a solid solution between $CoFe_2O_4$ and $FeCo_2O_4$, we aim to elucidate the relationship between the electronic (magnetic) state and crystal structure in connection with the chemical composition.

2. Experimental

Powdered crystals of $CoFe_2O_4$ were synthesized from 1:1 mixtures of CoO and Fe_2O_3. The mixtures were ground in an agate mortar, sealed in evacuated silica tubes, and heated at 1273 K for 24 hours. The products were ground again and heated for another 24 hours to achieve the complete chemical reaction. Powdered crystals of $FeCo_2O_4$ and $Fe_{1.5}Co_{1.5}O_4$ were synthesized by a method described by Martens *et al*. (1985). The respective 1:2 and 1:1 mixtures of $FeC_2O_4 \cdot 2H_2O$ and $CoC_2O_4 \cdot 2H_2O$ were prepared in an alumina crucible, very quickly heated up to 1173 K and maintained at the reached temperature for a week. Then, the crucible was quenched in water in order to prevent decomposition into two spinel-phases at intermediate temperatures. The products were ground again and then the same procedure was repeated. X-ray powder diffraction measurements were performed to examine for each of final products whether it was a single phase. As the results, all samples used in this study were single phases.

The XMCD experiments were performed at BL-3A of the Photon Factory using the phase shifter made of a thin diamond crystal, a rare-earth magnet (0.58 T) in the Faraday arrangement and two ionization chambers with N_2 (monitor) and 75% N_2 + 25% Ar gas. The difference in the absorption coefficients for right- and left-circularly polarized X-rays was measured with spin parallel and antiparallel in the direction of light travel. The storage ring was operated with the electron beam energy of 2.5 GeV and a maximum storage current of 500 mA. The horizontally polarized white X-rays were monochromatized by the Si(111) double-crystal monochromator. The beam was limited by 1 x 1 mm^2 at the sample position. The incident beam was guided into a synthetic single crystal of (001) diamond with a thickness of 0.492 mm in order to produce the circularly polarized X-rays which are irradiating the sample through a pinhole in the magnet. The scattering plane of the diamond crystal was selected to be inclined by 45° from the vertical plane in order to balance the σ and π components of a transmitted beam. The diamond crystal was set near the 111 Bragg condition in the asymmetric Laue case. In this study, we define the +90° (-90°) phase shift as a left (right) polarized X-rays which can be described as a clockwise (anticlockwise) rotation of electric field vectors against the direction of incident beam and magnetization. At each energy step, a right-polarized beam was first used and then switched. Associated with the switching• scheme, the monochromator angle was step-scanned toward the hi_her energy side.

The powder samples were prepared by mounting on a transparent tape. Several sheets of the tape were piled up to gain a thickness suitable for the best absorption and mounted on a sample holder of a goniometer head. The absorption intensities with left (+) and right (-) circularly polarized X-rays can be expressed as

$$\mu_c t = (1/2) [\ln I_0^+/I^+ - \ln I_0^-/I^-] \qquad (1)$$

where μ_c and t are a spin-dependent part of the absorption coefficient and sample thickness, respectively. The energy calibration was carefully made at the K-absorption edges using the pure metal foils.

3. Results and discussion

The spectra of X-ray absorption near edge structure (XANES) were obtained by the summation of left- and right-circular

polarization terms in the brakets of Eq. (1). Figure 1 shows the XANES spectra of cobaltite and ferrite at the Fe K and Co K absorption edges. The threshold energy of XANES spectra of
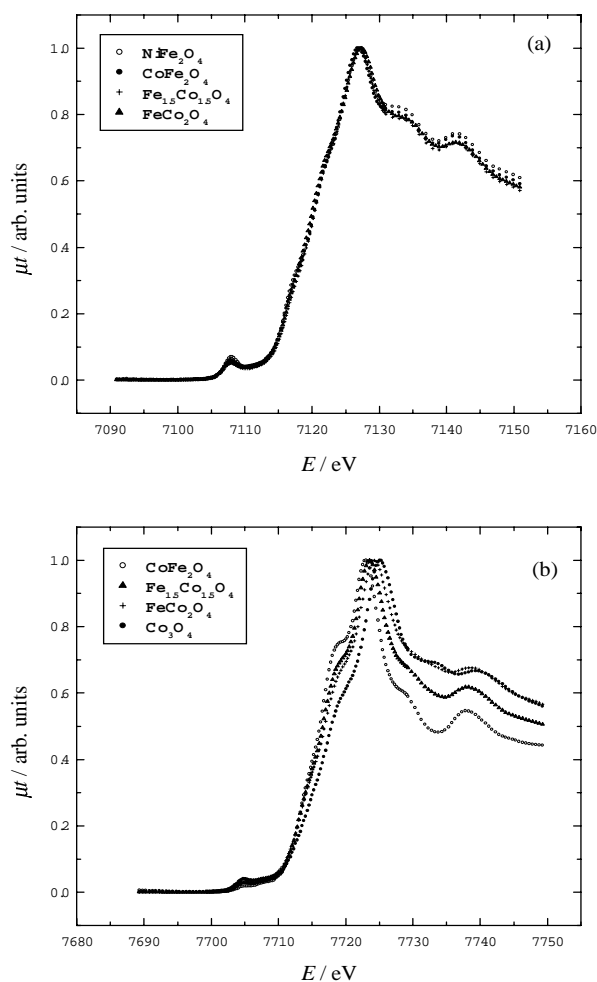
CoFe$_2$O$_4$, Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$ measured at the Fe K edge coincides with that of NiFe$_2$O$_4$ (Saito *et al*., 1999) in Fig. 1(a). In addition to the threshold of the absorption spectra, the total profile including the pre-edge structure closely resembled each other. Thus, the spectra indicate that iron ions in all compounds examined so far exist as trivalent ions, Fe^{3+}. In discussing somewhat more complicated cobaltites it is very important that only Fe^{3+} ions exist in CoFe$_2$O$_4$, Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$.

As shown in Fig. 1(b), the XANES spectra obtained at the Co K edge had the following characteristics. The threshold energy of the XANES spectra for Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$ are located at lower energy in Co$_3$O$_4$ spectra (Co$^{+2.67}$) but at higher energy than in the CoFe$_2$O$_4$ spectra (Co^{2+}). The conclusion is that Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$ contain both Co^{2+} and Co^{3+} ions. With the previous studies on the saturation magnetization measurements (Takahashi *et al*., 1971), catalytic activity (Goldstein and Tseung, 1973) and X-ray anomalous scattering (Yakel, 1980), the cation distributions were suggested in this

study to be [Fe^{3+}]^A[Co^{2+}Fe^{3+}]^{B}O$_4$, [Fe$_{0.75}$$^{3+}Co_{0.25}$$^{2+}$]^A [Fe$_{0.75}$$^{3+}Co_{0.75}$$^{2+}Co_{0.5}$$^{3+}$]^{B}O$_4$ and [Fe$_{0.6}$$^{3+}Co_{0.3}$$^{2+}Co_{0.1}$$^{3+}$]^A [Fe$_{0.4}$$^{3+}Co_{0.7}$$^{2+}Co_{0.9}$$^{3+}$]^{B}O$_4$ for CoFe$_2$O$_4$, Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$, respectively.
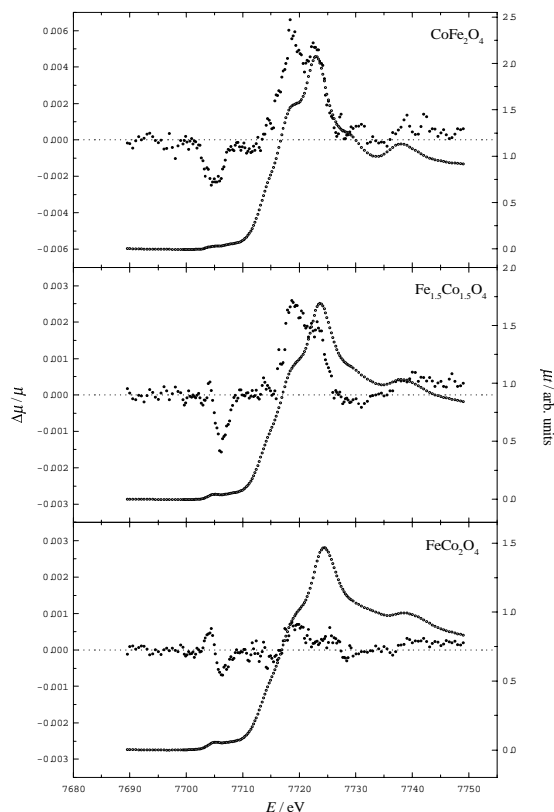
XMCD spectra were obtained based on Eq. (1). In spite of the difference in the Fe contents among CoFe$_2$O$_4$, Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$, the XMCD spectra recorded at the Fe K edge resembled each other in both pre- and main-edge regions (Fig. 2). The results support the interpretation that the XANES spectra can be overlapped. Therefore, it is suggested that the Fe^{3+} ions should have a similar electronic state regarding 3d and 4p orbitals in CoFe$_2$O$_4$, Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$.

The XMCD spectra at the Co K edge are shown in Fig. 3 for CoFe$_2$O$_4$, Fe$_{1.5}$Co$_{1.5}$O$_4$ and FeCo$_2$O$_4$, in comparison with the XANES spectra. The following characteristics were found at the Co K edge. (1) In the vicinity of the pre-edge, the concave patterns in CoFe$_2$O$_4$ changed to a dispersion-type signal in FeCo$_2$O$_4$. The XMCD spectrum of Fe$_{1.5}$Co$_{1.5}$O$_4$ has an intermediate pattern between the two. Co^{2+} should have a similar electronic configuration as Fe^{3+}. From the analogy of the pre-edge peaks in ferrites, it seems plausible that the pre-edge signal originates from the Co^{2+} ions of the A sites. (2) In the vicinity of the main-edge, the double peaks decreased in height

Figure 1

XANES spectra in the vicinity of (a) Fe K absorption edge and (b) Co K absorption edge
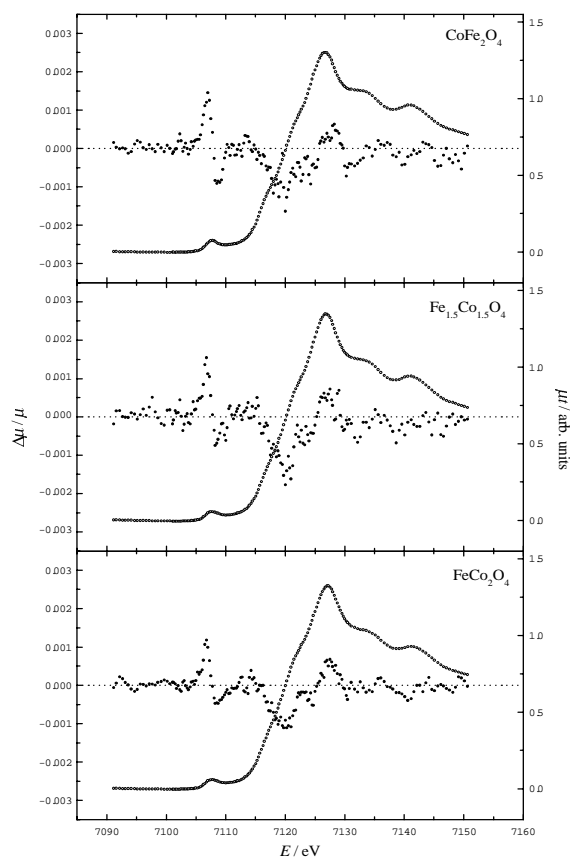
Figure 2

XMCD spectra of CoFe$_2$O$_4$, Co$_{1.5}$Fe$_{1.5}$O$_4$, FeCo$_2$O$_4$ in the vicinity of Fe K absorption edge.

dichroism

with the compositional change from $CoFe_2O_4$ to $FeCo_2O_4$. The peak position is around $E = 7720$ eV and invariant with the Co

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Figure 3
XMCD spectra of $CoFe_2O_4$, $Co_{1.5}Fe_{1.5}O_4$, $FeCo_2O_4$ in the vicinity of Fe *K* absorption edge.

content. The change at the main-edge can be explained by comparing the XMCD spectra of $NiCo_2O_4$. The origin of XMCD signals of $FeCo_2O_4$ at the main edge is Co^{2+} in the B sites, which has the trigonal symmetry. The XMCD spectra of $FeCo_2O_4$ at the Co K edge are quite similar but in inverse signs in the distribution to those of $NiCo_2O_4$ at the Ni *K* edge (Kita, 2000). It is known that the B sites of $NiCo_2O_4$ contain Ni^{3+} ions in the low-spin state. Because Co^{2+} and Ni^{3+} have the same d^7 electronic configuration, the Co^{2+} ions in the B sites of $FeCo_2O_4$ could be interpreted as having electronic states similar to Ni^{3+} in $NiCo_2O_4$. In conclusion, the Co^{2+} in the B sites of $FeCo_2O_4$ may prefer the low-spin states (^2E_g, $S = 1/2$) as well as Co^{3+} ($^1A_{1g}$, $S = 0$). On the other hand, Co^{2+} ions in the B sites of $CoFe_2O_4$ ferrite should be in a high-spin state ($^4T_{1g}$, $S = 3/2$). The intermediate XMCD patterns in the intermediate cobaltite of $Fe_{1.5}Co_{1.5}O_4$ could be explained by the existence of a mixture of high-spin and low-spin states of Co^{2+} in the B sites. There is a report on the possible existence of a second order high-spin to low-spin transition for the octahedral Co^{3+} ions of Co_3O_4 (Touzelin, 1978; Barabers and Broemere, 1992), although their thermoelectric measurements do not support the possibility of another electronic charge transition (Lenglet and Jørgensen, 1994).