

Mixing of Co^{2+} and Co^{3+} ions in $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ examined by XMCD and single-crystal X-ray diffraction

Norio SHIMIZU¹, Maki OKUBE¹, Koichi OHKUBO¹, Takayasu HANASHIMA¹,
Kouji YAMAWAKI¹, Takeharu MORI², Masahiko TANAKA², Satoshi SASAKI*¹
¹Materials and Structures Lab., Tokyo Inst. Tech., Nagatsuta, Yokohama 226-0803, Japan
²KEK-PF, Tsukuba, Ibaraki 305-0801, Japan

Introduction

The spinel structure, which has the geometrical frustration of a pyrochlore type, is attractive in the superexchange interaction between the A and B sites. Site occupancy between Fe and Co ions in ferrites and cobaltites is a key factor to control the physical properties. The occupancy can be determined accurately with the anomalous scattering effects of synchrotron X-rays. As well known, it is difficult to grow single crystals of cobaltites. Fortunately, we have succeeded to synthesize single crystals in the hydrothermal reaction. A combination study of X-ray diffraction, X-ray absorption near edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) makes it possible to determine the valence and spin states of Fe and Co ions of the mixed-valence compounds. Thus, in this study, the valence and spin states of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ spinels [1] have been examined.

Experimental

Synchrotron diffraction experiments for $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ were carried out in a four-circle diffractometry at BL-10A. The horizontally polarized white X-rays were monochromatized by the Si(111) monochromator. The wavelengths used in this study are 1.6182 Å near Co *K* absorption edge. As a total, the intensity data with 349 reflections were measured with ω - 2θ step.

XANES and XMCD experiments were carried out on the BL-3A. The X-ray beam from the Si(111) monochromator was limited to $3^{(\text{H})} \times 2^{(\text{V})}$ mm² at the sample position by a slit. The intensity after transmitting through the sample was measured with 300 mm ionization chamber which was filled with 75% N_2 + 25% Ar gas. The difference in the absorption coefficients for right- and left-circularly polarized X-rays was measured with spins parallel and antiparallel to the direction of light travel. The incident beam was guided into a synthetic single crystal of (001) diamond with a thickness of 0.492 mm in order to produce circularly polarized X-rays. A standard transmission setup was used with the Faraday arrangement, where X-rays irradiates the sample through a pair of pinholes in rare-earth magnets in a magnetic field of 0.4 T.

Results and discussion

The anomalous scattering method was used to determine the cation distribution between Fe and Co ions with a

large difference in atomic scattering factors. Least-squares refinements for an $\text{Fe}_{1.2}\text{Co}_{1.8}\text{O}_4$ sample gave a final chemical formula of $[\text{Fe}_{0.72}\text{Co}_{0.28}]^{\text{A}}[\text{Fe}_{0.48}\text{Co}_{1.52}]^{\text{B}}\text{O}_4$.

Co *K*-edge XANES and XMCD spectra of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ ($x = 0, 0.8, 1.0, 1.1, 1.4, 1.8, 2.0$ and 2.1) gave the compositional dependence on the valence state of Co ions. At the energy of the main edge, the XANES spectra has a chemical shift to move the higher region with the increase of Co contents. This accords with the contents occupied by Co^{3+} in $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$.

At the Co *K* edge, each of the XMCD peaks for the samples with $x < 1.4$ splits into two peaks of $E = 7707$ eV and $E = 7715$ eV. The boundary composition is close to $x = 4/3$, where Fe^{3+} , Co^{2+} and Co^{3+} ions occupy the B sites in the ratio of 1 : 1 : 1. The split of the XMCD peaks suggests a change of the Co spin state among the triangle B lattice of the spinel structure. The characteristics can be well compared with the compositional dependence of B-O interatomic distances.

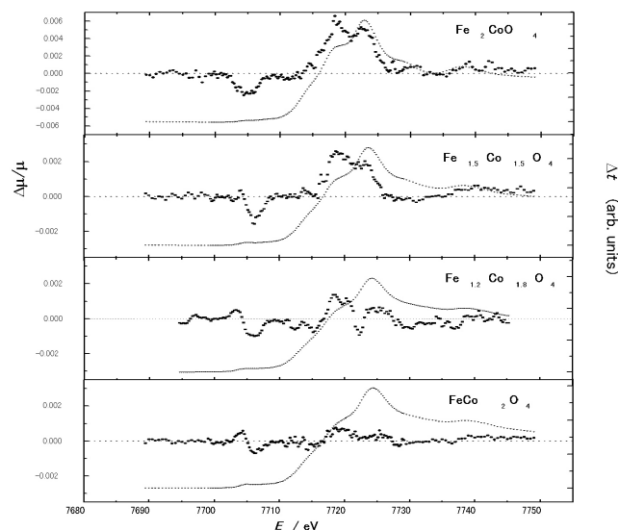


Fig. 1: XMCD spectra of $\text{Fe}_x\text{Co}_{3-x}\text{O}_4$ ($1 \leq x \leq 2$) at the Co *K* edge.

References

[1] N. Kita et al., *J. Synchrotron Rad.*, **8**, 446 (2001).

*sasaki@n.cc.titech.ac.jp