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Site-Specified Magnetic States in Ferrites Probed by Magnetic Circular X-Ray Dichroism

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Abstract. To study magnetic states in ferrimagnetic Fe-oxides, we have measured magnetic circular x-ray dichroism at *K*-edge of 3*d*-transition metal. The observed dichroic signals are separately assigned to the contribution come from 3*d*-cation in tetrahedral or octahedral sites. We discuss the magnetic states of 3*d*-metal ion in terms of local environment.

1. INTRODUCTION

Magnetic circular x-ray dichroism (MCXD) is a powerful technique for studying magnetic states in magnetic materials because of an element-specificity, a shell-selectivity, and an angular momentum sensitivity. To clarify the difference in magnetic states of 3*d*-transition metal (*M*) ions depending on local environment, *e.g.*, tetrahedral (*T_d*) or octahedral (*O_h*) symmetry, we have applied this technique to various Fe-oxide ferrimagnets with the spinel or garnet structure. In general, *K*-edge absorption spectrum in *M*-oxides is characterized by a pre-peak structure and an enhanced main-peak one around the edge. The pre-peak has been assigned to the *1s* → 3*d* dipole-allowed transitions in *T_d*-sites whereas the main-peak is properly related to the *1s* → 4*p* transitions [1]. In this report we distinguish between the contributions of *T_d* and *O_h* sites to the spectrum through the preferred substitution of *M*-ion in spinel and the difference in site-occupation between spinel and garnet. Hence, the magnetic states of *M*-ion are discussed in terms of crystal field and local symmetry.

2. EXPERIMENT

The Fe-oxides studied in this work include *M*Fe₂O₄ (*M*=Mn, Fe, Co, and Ni), γ-Fe₂O₃, and LiFe₅O₈ as spinel-type, R₃Fe₅O₁₂ (*R*=Y and Ho) as garnet-type, and BaFe₁₂O₁₉ as magnetoplumbite-type. MCXD spectrum was recorded in transmission mode for powder sample using the left-circularly polarized x-rays on BL-28B at Photon Factory 2.5 GeV storage-ring in KEK. The MCXD spectrum ($\Delta\mu t$) is defined as the difference in absorption with reversing the direction of magnetic field: $\Delta\mu t = [\mu t(\uparrow) - \mu t(\downarrow)]$, and x-ray absorption near-edge structure (XANES : μt) is shown as the average: $\mu t = [\mu t(\uparrow) + \mu t(\downarrow)]/2$, where \uparrow (\downarrow) represents the antiparallel (parallel) configuration of magnetic field with respect to the wave vector of incident x-ray. The MCXD spectrum was systematically measured at the *K*-edge of Mn, Fe, Co, and Ni.

3. RESULTS AND DISCUSSION

Fe *K*-edge XANES and MCXD spectra are shown in Figures 1(a) and 1(b), respectively. In the case of inverse spinel, the substitution of Co²⁺, Ni²⁺, Li⁺ ion, or defect for Fe²⁺ in *O_h*-sites causes scarcely any change in the XANES spectrum; on the other hand, in the case of Mn-ferrite with the normal spinel structure, the substitution of Mn²⁺ ion for Fe³⁺ in *T_d*-sites induces a significant reduction of pre-peak intensity. On the contrary, in the garnet-type ferrite including more *T_d*-sites, the pre-peak intensity clearly increases in comparison with that in spinel. These observations are in good agreement with the assignment that the pre-peak is attributed to the cations in *T_d*-sites. It is not clear, however, whether the main-peak can be associated with the *O_h*-sites or not, because its feature is spread over the large continuum background resulting from the *1s* → 4*p* dipole transitions.

To clarify this, magnetic effect in XANES spectrum, *i.e.*, dichroic signal, will be effectual, because it provides the information on magnetic polarization in the interesting electronic states. Figure 1(b) shows the Fe *K*-edge MCXD in this series. The observed spectrum is formed a remarkable dispersion-type profile and located in both the pre-peak (~ 0 eV) and the main-peak (~ 15 eV) regions. In Mn-ferrite, the dichroism almost disappears in the pre-peak region but yields prominent spectrum at the main-peak position. In the other ferrites, the intensity ratio of MCXD at main-peak to that at pre-peak is consistent with the substitution for the Fe ion in *O_h*-sites. In garnet ferrite, the dispersion-type dichroic signal is clearly observed only in the pre-peak region and shows an opposite sign to that in spinel, which is interpreted as the magnetic site dominantly contributed to bulk magnetization in ferrimagnet. Harada and Kotani [2] have theoretically reproduced the dispersion-type dichroic spectrum of Fe³⁺ ion in the *T_d*- or *O_h*-symmetry by taking *p* - *d* hybridization with O²⁻ ligands and spin-orbit coupling in *t_{2g}* orbitals into account. We

can associate the dichroism in the main-peak region with Fe ion in O_h -sites. However, a subtle MCXD signal in the main-peak region in garnet is still an open question.

To verify our assignment, moreover, we have measured XANES and MCXD spectra concerning the substituted M-ion in spinel. Figures 2(a) and 2(b) show the Co and Ni K -edge spectra, respectively. In XANES, the spectra exhibit an enhanced white-line like absorption and a substantial reduction of pre-peak intensity. In MCXD, a positive-double-peak appears at the position corresponding to the white-line like absorption, and no dichroic signal at the pre-peak is observed. These experimental facts demonstrate that the magnetic Co^{2+} or Ni^{2+} ion is preferably substituted for the Fe^{2+} ion in O_h -sites. The similarity between the Co and Ni MCXD spectra may be related to a resemblance of local magnetic states in such divalent ion in spite of the difference in the ground-state $3d$ -electronic configurations. Although there is no interpretation of such positive-double-peak dichroic spectrum, it is associated with crystal-field splitting, exchange interaction, charge-transfer, $p-d$ hybridization, etc. For the Mn K -edge, the characteristic dispersion-type spectrum is expected because of the same $3d^5$ electronic configuration as the Fe^{3+} ion. Actually, such dichroic signal is observed in a wide region of the edge, so that the structure is very complicated and possibly related to the inverse spinel structure. Consequently, we conclude that the dichroic signal in the main-peak region is reasonably attributed to Fe ion in O_h -sites.

Let us briefly discuss the magnetic states of Fe^{3+} ion in terms of crystal field and local symmetry. The dichroism can be interpreted as the mechanism [2] composed of the dipole-allowed $1s \rightarrow 3d$ transitions, which is due to the hybridization between Fe $3d$ and ligand $2p$ orbitals, and the spin-orbit coupling in the $3d$ -states, which leads to a splitting in the degenerated t_{2g} and e_g multiplets. Hence, the MCXD is very sensitive to the local environment of polyhedron. The ground state electronic configurations of the cation in O_h -symmetry studied in this work are in a high-spin state, so that the dichroism for the substituted cations range from Mn($3d^5$) to Ni($3d^8$) is essentially related to the electron-filling of the $3d$ t_{2g} -states.

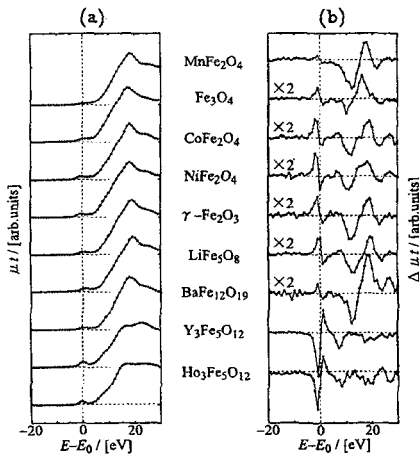


Figure 1: (a) XANES and (b) MCXD spectrum at the Fe K -edge. Absorption edge energy E_0 was determined as the position of the pre-peak structure, which is constant regardless of the samples within the experimental error.

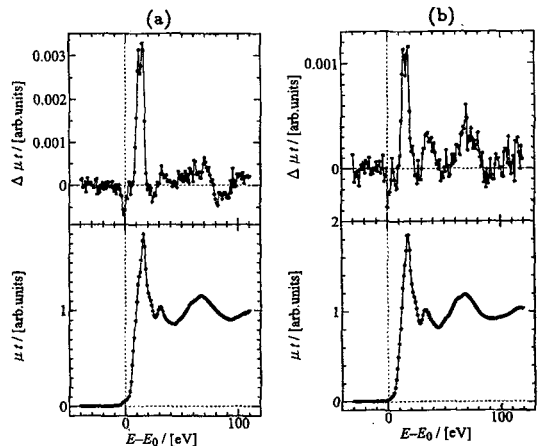


Figure 2: XANES (lower panel) and MCXD (upper panel) spectra (a) at the Co K -edge in Co-ferrite and (b) at the Ni K -edge in Ni-ferrite.

4. CONCLUSION

We have measured the XANES and MCXD spectra at K -edge of Mn, Fe, Co, and Ni in the various ferrimagnetic oxides with the spinel or garnet structure. For the Fe K -edge spectra, we have verified that the pre-peak (main-peak) structure is attributed to the cations in T_d (mainly O_h) sites, through the preferred substitution in spinel and the difference in site-occupation between spinel and garnet. Since the MCXD is very sensitive to the local environment of polyhedron, it is useful for studying the magnetic states of $3d$ -ions in a local symmetry.

Acknowledgments

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References

- [1] L.A. Grunes, Phys. Rev. B **27**(1983) 2111-2131.
- [2] I. Harada and A. Kotani, J. Phys. Soc. Jpn. **63**(1994) 1285-1288.