Magnetic Electron-Density Distribution in Magnetite Determined by RXMS Difference-Fourier Method

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Introduction

Resonant X-ray magnetic scattering (RXMS) is a useful tool to examine the magnetic structures associated with specific electronic states such as $3d$-$4p$ interactions. Although various magnetic resonant experiments have been carried out [1-3], there is no report on the crystallographic study on the magnetic electron density for the use of all Bragg reflections and Fourier synthesis. Our RXMS study has been focused on the observation of magnetic electrons in magnetite Fe_3O_4, where there are Fe^{3+} ions in tetrahedral A and octahedral B sites and Fe^{2+} in B sites.

Experimental

The crystal used in this study was provided by Drs. S. Todo and H. Kawata. A spherical crystal of 0.13 mm in diameter was mounted along the a_3 axis on the glass fiber on a rare-earth magnet in a magnetic field of 0.14 T. Synchrotron RXMS experiments were performed at the BL-6C beamline using a conventional Rigaku AFC5 four-circle diffractometer. The linearly polarized x-rays were monochromatized by a Si(111) double-crystal monochromator and transformed to edge, which were introduced into circularly polarized ones by a transmission-type x-ray phase retarder of (001) diamond. The wavelength is selected at the Fe K absorption as $\lambda = 1.7442$ Å ($E = 7.1082$ keV), based on a positive peak in the dispersive XMCD signal at the pre edge.

The intensity was measured with the left- and right-polarized x-rays and normalized with a total integrated intensity. The intensity correction for each reflection was made for background intensity, scaling and angle-dependent polarization effect. The least-squares calculations to obtain the calculated structure factors were made by using least-squares software RADY.

Results and discussion

The calculation of the difference in crystal structure factors between left- and right-circular polarized measurements makes it possible to perform a difference-Fourier synthesis for targeting only magnetic electrons within energy resolution of 0.5 to 1 eV. The difference-Fourier synthesis is superior in examining the magnetic effect in the polarization difference and eliminating the other effects such as charge scattering and experimental errors. It is also effective in removal of the termination

effect of Fourier series. In the Fourier series, the difference in the electron density can be finally written as

$$\Delta\rho(\boldsymbol{r})^{\mathrm{spin}} = \frac{1}{V}\Sigma\Sigma\Sigma\{|F_{\mathrm{obs}}(hkl)^{E,\mathrm{left}}| - |F_{\mathrm{obs}}(hkl)^{E,\mathrm{right}}|\}\exp(-2\pi\mathrm{i}\,\boldsymbol{k}\cdot\boldsymbol{r}).$$

Difference-Fourier syntheses were then made in triclinic symmetry by using the software FRAXY. Figure 1 shows the difference-Fourier map of Fe_3O_4 on the plane passing through $x_3 = 1/2$, which was synthesized using the difference $[\Delta\rho_{\mathrm{obs}}(\boldsymbol{r})^{\mathrm{left}} - \Delta\rho_{\mathrm{obs}}(\boldsymbol{r})^{\mathrm{right}}]$. A positive peak was observed in the B site, which requires the contribution from the quadrupole transition or the hybridization among neighboring ions. The negative residual densities appear apart from the B-O bond, which may suggest the existence of the A-O-B superexchange interaction of magnetite through the hybridization of Fe and oxygen atoms.
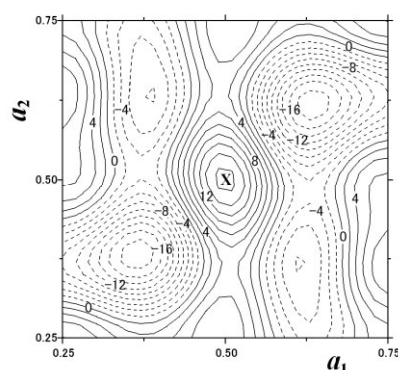

Fig. 1: Magnetic electron-density map in e/Å³ units for the B site on (h_1h_20) within $1/4 \leq x \leq 3/4$. The B site locates at the position "X" of (1/2,1/2,1/2). Contours are at intervals of 0.04 e/Å³, where the numbers in maps are magnified by 50. Solid lines are zero and positive contours and broken lines are negative contours. The scaling of the electron density is not absolute because of the use of F_{calc}.

References

[1] K. Namikawa et al., J. Phys. Soc. Jpn. 54, 4099 (1985).
[2] D. Gibbs, J. Magn. Magn. Mater. 104-7, 1489 (1992).
[3] S. Ohsawa et al., AIP Conf. Proc. 879, 1715 (2007).

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