Crystallography

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Electron-Density Mapping on X-Ray Resonant Scattering for Fe Sites of Magnetite

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Introduction

It is interesting to pinpoint specific atoms by extracting some electrons resonantly scattered. For example, the position of 1*s* electrons can be estimated from the *shell structure factors* to be the balance between X-ray resonant scattering (XRS) and total intensity [1]. Recently, the electron-density analysis of magnetite has revealed the overlapping of magnetic electron orbitals among neighboring atoms, by making use of the intensity difference in resonant X-ray magnetic scattering between left- and right-circular polarizations [2]. Magnetite has the crystal structure of inverse-spinel type of $[Fe^{3+}]^A[Fe^{2+}Fe^{3+}]^BO_4$, where only Fe^{3+} occupy the tetrahedral A sites and Fe^{2+} and Fe^{3+} occupy equally the octahedral B sites. It is known that in X-ray absorption experiments magnetite has a pre-edge structure at the Fe *K* edge. Although the pre-edge peak is considered as a dipole-transition mechanism of Fe^{3+} in the tetrahedral sites, the site symmetry of the octahedral sites is .-3*m* and gives another possibility on the origin with super-exchange interaction of A-O-B.

Experimental

Magnetite used in this study has a cell dimension of a = 8.4000(3) Å with the space group of *Fd*-3*m*. Synchrotron experiments were performed at BL-6C and BL-10A of the Photon Factory using a conventional Rigaku AFC5 and vertical-type four-circle diffractometers, respectively. In the BL-6C experiments, Si(111) double-crystal monochromator and diamond(001) phase retarder were used to produce circularly polarized X-rays at the Fe *K* edge. Intensity data for 354 reflections were collected in the range $2\theta \leq 90°$ with an ω-2θ step scan mode.

Results and discussion

The difference-Fourier synthesis between two sets of observed data was applied to X-ray resonant scattering (XRS). The XRS effect measured at a pre-edge of Fe *K* absorption edge makes it possible to give the information on a location of electrons resonantly scattered and therefore, of targeted atoms. The electron density can be estimated to subtract the resonant intensity at the pre-edge from off-edge intensity. Using a difference in the XRS pre-edge intensity measured at energy E_{on} and E_{off}, a difference in electron-density is given by $\Delta\rho(\boldsymbol{r}) = V^{-1} \Sigma\Sigma\Sigma\{F(hkl)_{on}\text{-}F(hkl)_{off}\}\exp(-2\pi i\boldsymbol{k}\cdot\boldsymbol{r})$, where $F(hkl)$ and $\boldsymbol{k}$ are the crystal structure factor and scattering vector, respectively, and then the termination effect of Fourier series is automatically corrected.

Figure 1 shows the electron-density maps of magnetite on the planes passing through (a) A and (b) B sites, respectively. Contours are at intervals of 0.5 e/Å^3, where the numbers in maps are magnified by 10 and solid lines are zero and positive and broken lines are negative. Negative peaks appear around A and B sites in heights of -2.7 and -2.9 e/Å^3, respectively. It is concluded that the origin of the pre-edge peak of magnetite should be both of A and B sites.

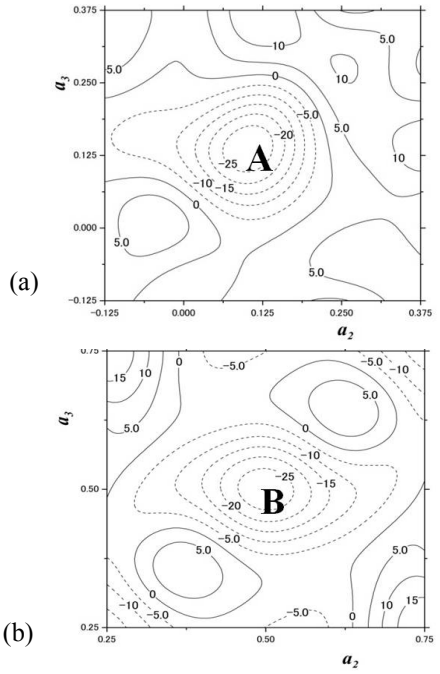

Fig. 1: Electron-density maps in e/Å^3 units for (a) A site on ($0h_2h_3$) within -1/8 ≤ x ≤ 3/8 and (b) B site on ($0h_2h_3$) within 1/4 ≤ x ≤ 3/4. The A and B sites locate at (1/8,1/8.1/8) and (1/2,1/2,1/2), respectively. Contours are at intervals of 0.5 e/Å^3, where the numbers in maps are magnified by 10. Solid lines are zero and positive contours and broken lines are negative contours.

References

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