Accurate determination of anomalous scattering factor near Fe K absorption edge

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Abstract. When X-ray energy is close to the absorption edge, the anomalous scattering factor changes drastically and the determination of the real part \(f'(E)\) becomes important for crystal-structure analyses. The resonant X-ray diffraction technique has been applied to distinguish crystallographically independent sites of magnetite (Fe\(_3\)O\(_4\)), which has the inverse-spinel structure with tetrahedral A and octahedral B sites. In this study, we have site-selectively estimated \(f'\) values for the different Fe sites by using X-ray diffraction data measured at Fe K edge. The intensity data were collected at two X-ray energies, \(E_{on}\) (=7.1082 keV) and \(E_{off}\) (=7.1051 keV), corresponding to on- and off-peaks of the Fe pre-edge. Through the least-squares calculation to refine \(f'(E)\) as an unknown parameter, the \(f'(E)\) values of Fe\(^{3+}\) for A and B sites were determined to be -7.680 and -7.855 at \(E_{on}\) and -6.682 and -6.709 at \(E_{off}\), respectively. These values are in a good agreement with -7.943 for total Fe ions, obtained from the absorption data of NiFe\(_2\)O\(_4\) in the inverse-spinel structure.

1. Introduction
X-ray Bragg intensity depends on the scattering power of atoms described by atomic scattering factors \(f\). It is essential to use such factors for X-ray diffraction study and crystal-structural analysis. When X-ray energy \(E\) is close to the absorption edge of an element, the resonant effect becomes dominant between incident X-rays and electrons of the constituent atoms [1]. Then, \(f\) includes the dispersion terms called “X-ray anomalous scattering” or “X-ray resonant scattering (XRS)”. The atomic scattering factor reflects the electronic state and is extendedly expressed with complex terms of \(f = f_0 + f'(E) + if''(E)\). \(f_0\) is Thomson elastic scattering, \(f'(E)\) and \(f''(E)\) are real and imaginary parts of the anomalous scattering factor. Since the anomalous dispersion occurs near the absorption edge, it is useful to highlight a particular kind of atom in a crystal.

A real part \(f'(E)\) can be calculated from the relativistic wave functions [2]. Although the theoretical calculation of the anomalous scattering factor is limited for an isolated free atom, the factor in a real crystal is attributed to the scattering power from target atoms affected by the surroundings. There is a discrepancy between theoretical and experimental values. Many attempts have been made near an absorption edge to measure \(f'(E)\) or \(f''(E)\) by various X-ray techniques [3-7]. The use of the dispersion relation of the Kramers-Kronig integral is a realistic way to determine \(f'(E)\) because of the ordinary measurements [8,9]. Figure 1 shows \(f'(E)\) and \(f''(E)\) of NiFe\(_2\)O\(_4\). The imaginary term \(f''(E)\) is related to the absorption coefficient which is derived from XANES spectrum of NiFe\(_2\)O\(_4\). The real
term $f'(E)$ is calculated from $f''(E)$ by the Kramers-Kronig dispersion relation [10]. The pre-edge feature of XANES is clearly observed in $f'(E)$ of Fig. 1, which is sensitive to the oxidation state and local chemical environment. Since the theoretical values of $f'(E)$ are limited to calculate only for an isolated atom, more accurate value for practical use is needed especially in the energy region close to the absorption edge. However, a spectroscopic study of absorption gives only overall information averaged on the element. In the case when a kind of atoms occupies two or more crystallographic sites in different coordination numbers, $f'(E)$ becomes unreliable. Therefore, it is significant to provide site-specific and individual $f'(E)$.

**Figure 1.** Energy dependence of anomalous scattering factors of NiFe$_2$O$_4$. Lower and upper figures are related in the Kramers-Kronig dispersion. The data collection were made at $E_{\text{on}}$ ($= A$) and $E_{\text{off}}$.

Magnetite Fe$_3$O$_4$ is ferrimagnetic and of inverse-spinel type with the space group of $Fd-3m$ (Fig. 2). The chemical formula is $[\text{Fe}^{3+}]^6[\text{Fe}^{2+}\text{Fe}^{3+}]^2\text{O}_4$, where Fe occupies tetrahedral A and octahedral B sites. In this study, through the measurement of X-ray resonant scattering in the Fe $K$ pre-edge, anomalous scattering factors of Fe have been determined site-independently. A related article has been published elsewhere [11]. Since the result on $f'(E)$ depends on the probability of electron transition, our approach would contribute to the quantitative discussion on the electronic states in magnetite.

2. **Experimental**

All synchrotron experiments were performed at BL-6C of the Photon Factory. The XANES measurements of magnetite and NiFe$_2$O$_4$ were made near the Fe $K$ edge using two ionization chambers filled with N$_2$ and 85% N$_2$ + 15% Ar gas. The XANES curve of magnetite is shown in Fig. 3, which is well compared with that of NiFe$_2$O$_4$ given in Fig. 1. The feature of pre-edge peak of both crystals is similar each other. X-ray energies of $E_{\text{on}}$ ($= A$) and $E_{\text{off}}$, marked only in Fig. 1, were selected for the diffraction measurements.

Resonant X-ray scattering measurements were carried out in the top-up operation mode of the storage ring using a Rigaku AFC-5 diffractometer. A spherical single crystal of magnetite was 0.13 mm in diameter and used for the data collection. The cell dimension determined is $a = 8.4000(3)$ Å.
a total, 354 reflections were measured up to \( \sin \theta \lambda = 0.4 \) within a range of \(-6 \leq h_1, h_2, h_3 \leq 6\). The intensity corrections on reflection data were made for Lorentz, polarization and spherical absorption effects prior to crystal-structure analyses. The reflections having \( F \geq 3\sigma(F) \) were averaged among all symmetrical equivalent reflections. Crystal-structure analyses with isotropic extinction correction [12] were carried out using a full-matrix least-squares program RADY [13]. In the refinement procedure, atomic coordinates and anisotropic temperature factors were first refined with the Mo \( K\alpha \) data set previously collected in laboratory. Then, anomalous scattering factors were determined with the resonant scattering data at the Fe \( K\alpha \) edge. Final \( R \) and \( wR \) factors for the \( E_{\text{on}} \) refinements were 0.048 and 0.057, while the factors for \( E_{\text{off}} \) were 0.050 and 0.061, respectively.

**Figure 2.** The crystal structure of magnetite, Fe\(_3\)O\(_4\). The A and B sites are tetrahedral (red) and octahedral (blue), respectively.

**Figure 3.** XANES spectrum of magnetite. The energy \( E_{\text{on}} \) and \( E_{\text{off}} \) used for X-ray diffraction measurements are indicated in Fig. 1.

### 3. Estimation of anomalous scattering factor \( f'(E) \)

Since magnetite contains both Fe\(^{2+}\) and Fe\(^{3+}\) in the structure, NiFe\(_2\)O\(_4\) was selected as an Fe\(^{3+}\) standard because of the same inverse-spinel structure. Accordingly, XANES spectrum of NiFe\(_2\)O\(_4\) was used to estimate \( f'(E) \) (Fig. 1). The real term \( f'(E) \) of Fe\(^{3+}\) was calculated from the imaginary term \( f''(E) \) by the program DIFFKK [10]. The values obtained in this study for \( f'(E) \) and \( f''(E) \) are -6.206 and 0.420 at \( E_{\text{on}} \) and -5.844 and 0.374 at \( E_{\text{off}} \), respectively (Table 1).

The multiplicity of \( f'(E) \) was refined with a scale factor in the best fit of the least-squares calculation, minimizing the sum of squared residuals in a function \( \sum w( |F_{\text{obs}}| - |F_{\text{calc}}| )^2 \). Figure 4 shows the best-fitting result for A and B sites, where the intensity data were measured at \( E_{\text{on}} \) and \( E_{\text{off}} \). In each case of the fitting, the variation of residual factors has a minimum against parameter \( f'(E) \), indicating a good convergence. The values thus estimated for \( f'(E) \) of the A and B sites are -7.063 and -6.971 at \( E_{\text{on}} \) and -6.682 and -6.709 at \( E_{\text{off}} \), respectively. It should be noted that the values for the two sites are almost identical, having a slight difference to be more negative for the A site. The differences between \( f'(E)_{\text{on}} \) and \( f'(E)_{\text{off}} \) are -0.381 and -0.262 for Fe occupying the A and B sites, respectively.

| \( E \) (keV) | \( \lambda \) (Å) | \( f' \) (A site) | \( f' \) (B site) | \( f' \) (K-K transform) |
|-------------|-------------|----------------|----------------|----------------------|
| \( E_{\text{on}} \) 7.1082 | 1.7442 | -7.063 | -6.971 | -6.206 |
| \( E_{\text{off}} \) 7.1051 | 1.7449 | -6.682 | -6.709 | -5.884 |
4. Conclusion
We have determined $f'(E)$ values site-selectively for two kinds of Fe sites by using X-ray resonant scattering method at the pre-edge of Fe $K$ absorption. The $f'(E)$ values of Fe$^{3+}$ for A and B sites are -7.680 and -7.855 at $E_{on} = 7.1082$ keV and -6.682 and -6.709 at $E_{off} = 7.1051$ keV, respectively.

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References
[1] James R W 1948 *The Optical Principles of the Diffraction of X-Rays* (Crystalline State Vol. II)
[2] Cromer D T and Liberman D A 1970 *J. Chem. Phys.* 53 1891
[3] Bonse U and Materlik G 1976 *Z. Phys. B* 24 189
[4] Fukamachi T and Hosoya S 1975 *Acta Crystallogr. A* 31 215
[5] Fukamachi T, Hosoya S, Kawamura T, Hunter S and Nakano Y 1978 *Jpn. J. Appl. Phys.* 17-2 (Suppl.) 326
[6] Fontain A, Warburton W K and Ludwig K F 1985 *Phys. Rev. B* 31 3599
[7] Templeton D H and Templeton L K 1980 *Acta Crystallogr. A* 36 436
[8] Fukamachi T, Hosoya S, Kawamura T and Okunuki M 1977 *Acta Crystallogr. A* 33 54
[9] Hoyt J J, Fontaine D and Warburton W K 1984 *J. Appl. Crystallogr.* 17 344
[10] Cross J O, Newville M, Rehr J J, Sorensen L B, Bouldin C E, Watson G, Gouder T, Lander G H, Bell M I 1998 *Phys. Rev. B* 58 11215
[11] Okube M, Yasue T and Sasaki S 2012 *J. Synchrotron Rad.* 19 759
[12] Becker P J and Coppens P 1974 *Acta Cryst.* A 30 129
[13] Sasaki S 1987 *RADY*: A FORTRAN Program for the Least-Squares Refinement of Crystal Structures (KEK Internal, National Laboratory for High-Energy Physics, Jpn.) 87-3 1

Figure 4. Variation of residual factors $\Sigma w(|F_{obs}| - |F_{calc}|)^2$ as a function of $f'(E)$. The least-squares calculations were made site-independently for A and B sites (solid and open circles), using the intensity data at energies $E_{on}$ (bottom) and $E_{off}$ (top) near Fe $K$ pre-edge.