

## Evidence of charge ordering of Fe<sup>2+</sup> and Fe<sup>3+</sup> in magnetite observed by synchrotron X-ray anomalous scattering

TAKESHI TOYODA,<sup>1</sup> SATOSHI SASAKI,<sup>1,\*</sup> AND MASAHIKO TANAKA<sup>2</sup>

<sup>1</sup>Materials and Structures Laboratory, Tokyo Institute of Technology, Nagatsuta 4259, Midori, Yokohama 226–8503, Japan

<sup>2</sup>Photon Factory, National Laboratory for High-Energy Physics, Oho, Tsukuba 305–0801, Japan

### ABSTRACT

Synchrotron anomalous scattering experiments with X-ray wavelengths at the Fe *K* absorption edge have made it possible to distinguish between ions having different valence states in magnetite at low temperatures. Using a large difference in anomalous scattering factors between Fe<sup>2+</sup> and Fe<sup>3+</sup>, the valence-difference contrast method was applied for the intensity measurements of fundamental and superlattice reflections of magnetite at low temperature. Reflections with half-integer indices, such as 0 4 ½ and 4 4 ½, were observed at 102 K, showing that magnetite transformed to a lower symmetry form. The energy dependence in the diffracted intensity was clearly observed at the Fe *K*-edge for the 0 4 ½ superlattice reflection at 102 K. A sharp minimum of the normalized intensity at  $E = 7.122$  keV was explained by the valence contrast between Fe ions occupied in the respective upper and lower parts of the double cell. Thus, our results strongly suggest the existence of charge ordering between ferrous and ferric ions in magnetite at low temperatures.

### INTRODUCTION

X-ray anomalous scattering techniques using tunable synchrotron radiation are suited for determining the electronic structure of a crystal. The X-ray atomic scattering factor can be described as  $f = f_0 + f' + if''$  where  $f_0$  is the Thomson scattering term and  $f'$  and  $f''$  are real and imaginary parts of anomalous scattering factors, respectively. At the energy region of the X-ray absorption near-edge structure (XANES), the change of the energy levels in electrons gives a chemical shift up to several eV between different oxidation states. The chemical shift is about 5 eV between Fe<sup>2+</sup> and Fe<sup>3+</sup> ions that are octahedrally coordinated O atoms. Absorption by the resonant element is related to  $f''$ , whereas  $f'$  can be theoretically transformed from  $f''$  by a Kramers-Kronig relation. A breakthrough on valence contrast studies appeared when the anomalous scattering factors were calculated from the observed absorption data with relatively accurate values for X-ray beams and crystals. Many attempts have been made with X-ray diffraction analysis for mixed-valence compounds such as Eu<sub>3</sub>O<sub>4</sub> (Attfield 1990), YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+x</sub> (Kwei et al. 1990), GaCl<sub>2</sub> (Wilkinson et al. 1991),  $\alpha$ -Fe<sub>2</sub>PO<sub>5</sub> (Warner et al. 1992), ( $\mu$ -dioxo Mn-(2,2'-bipyridyl)<sub>2</sub> (BF<sub>4</sub>)<sub>3</sub>·3H<sub>2</sub>O (Gao et al. 1992), and NbSe<sub>3</sub> (Gao et al. 1993). Specifically,  $f'$  at  $\lambda = 1.7415$  Å is remarkably different for having the values of  $-9.07$  and  $-7.10$  for Fe<sup>2+</sup> and Fe<sup>3+</sup>, respectively (Sasaki 1995).

Because the X-ray determinations depend on differences in atomic scattering factors, a large difference in  $f'$  allows oxidation states to be distinguished with higher

accuracy in the valence-difference contrast (VDC) method. This relatively new technique to survey different oxidation states has high potential for determining an electronic structure but its accuracy during practical use remains in dispute. An effective and direct use of the VDC method was reported on the observation of the diffuse scattering related to the valence fluctuation in magnetite, Fe<sub>3</sub>O<sub>4</sub> (Toyoda et al. 1997). The VDC method can clearly distinguish Fe<sup>2+</sup> ions from Fe<sup>3+</sup> in X-ray diffuse intensities at the Fe *K* absorption edge. On the iso-diffusion surface around a 440 reciprocal lattice point of magnetite at  $\lambda = 1.7425$  Å, the horn-like diffuse streak pattern elongating along the [110]\* was clearly observed at 150 K but disappeared at room temperature. Similar diffuse streaks were reported in neutron and electron diffraction (Shapiro et al. 1976; Chiba et al. 1975) but origin of the streaks differ from the X-ray case. The neutron diffuse streaks were interpreted by introducing a molecular polaron model with the local displacement of O atoms (Yamada et al. 1979). The X-ray diffuse streaks, which disappeared when the valence contrast was removed, were explained as a partial charge ordering of Fe<sup>2+</sup> and Fe<sup>3+</sup> in the ratio of 1:3 (or 3:1) along [110] (Toyoda et al. 1997).

High electric conductivity of magnetite at room temperature is due to hopping in a mixed-valence state where the continuous interchange of electrons exists between Fe<sup>2+</sup> and Fe<sup>3+</sup> in the B sites. As the result of freezing of the electron hopping, magnetite transforms to a lower symmetry form below the Verwey transition temperature ( $T_v \cong 123$  K). Although the low-temperature transition is a typical metal-insulator one, understanding of the tran-

\* E-mail: sasaki@n.cc.titech.ac.jp

sition as a result of research presented here is incomplete. The atomic structure of low-temperature magnetite as well as the lattice distortion accompanied by valence fluctuation are needed. Between region from  $T_v$  to 200 K where the heat-capacity anomaly occurs, the character of carriers has been studied with precursors, such as the diffuse scattering, as mentioned. The frequency of the fluctuation was estimated to be on the order of 1 THz just above  $T_v$ , to equal the frequency of charge fluctuation (Shapiro et al. 1976).

An ordering scheme where  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions were thought to alternate along the  $c$  axis resulting in 002-type reflection was proposed for low-temperature magnetite by Verwey et al. (1947). Although such extra reflections were not detected, Samuelsen et al. (1968) and Yamada et al. (1968) observed superlattice  $h0l/2$  type reflections by neutron and electron diffraction, respectively. Since then, several structural models for the low-temperature phase have been proposed as with rhombohedral, orthorhombic, monoclinic, or triclinic cells (Iizumi et al. 1982). Complicate twinning below  $T_v$  may cause the ambiguity on the crystal structure of low-temperature magnetite.

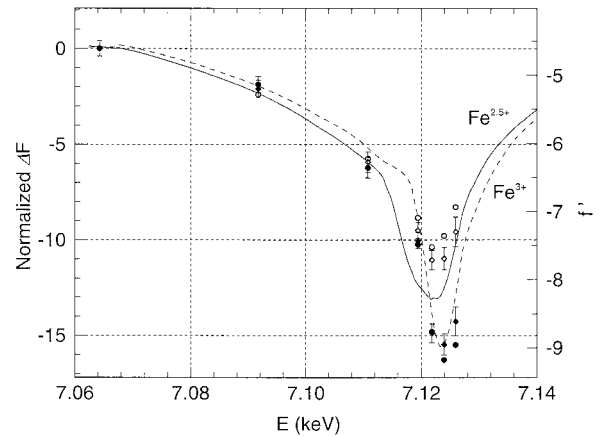
This paper demonstrates application of VDC methods on X-ray charge scattering to examine the valence fluctuation and low- $T$  phase transition of magnetite. Using wavelength-dependent diffraction and scattering studies of magnetite at the Fe  $K$ -edge, examination focused on charge ordering in the mixed valence compound.

### EXPERIMENTAL METHODS

Single crystals of magnetite were synthesized from  $\text{Fe}_3\text{O}_4$  powders either (1) in the 5 M  $\text{NH}_4\text{Cl}$  solution in gold tube at 673 K or (2) in Pt-10% Rh crucible by the Bridgman method in the  $\text{CO-CO}_2$  atmosphere. A spherical crystal of 0.12 mm in diameter was used for the crystal structure analysis at room temperature, whereas, parallelepiped crystals up to 0.2 mm in a length were used for low- $T$  X-ray studies.

Synchrotron experiments were performed at the BL-10A of Photon Factory using a vertical-type four-circle diffractometer. An Si(111) monochromator was used in horizontal dispersion to select a special wavelength near the Fe  $K$ -edge. First, X-ray intensity measurements were performed at room temperature to check the validity of the VDC method using seven wavelengths at the vicinity of the Fe  $K$ -edge: 1.7399, 1.7404, 1.7409, 1.7415, 1.7436, 1.7483, and 1.7551 Å. The X-ray wavelengths were calibrated with the absorption spectra of 5  $\mu\text{m}^2$  iron foil and FeO powders. The standard in energy used was 7.1196 keV, which corresponded to the second inflection point of the absorption curve of FeO (Sasaki 1995) and was related to 7.1120(9) keV at the first inflection point of Fe foil (Bearden and Burr 1989). Intensity profile data around the Bragg reflections were collected at the  $\omega$ -2 $\theta$  step scan mode.

Low- $T$  experiments were performed by blowing cold and dry nitrogen gas directly onto the crystal. The tem-



**FIGURE 1.** Energy dependence of crystal structure factors for the spinel phase of magnetite. The 222 reflection = open circle and 226 reflection = open square reflections are mainly affected by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  of the B sites, whereas the 026 solid circle and 246 solid square involve only  $\text{Fe}^{3+}$  in the A sites. For example, a difference in anomalous scattering for 222 can be normalized as:  $f' - f'_s \cong [F(222) - F_s(222)]/4$ , where  $f' = f'_s$  for oxygen  $f_o = f_{os}$  and  $f''$  differences are neglected. The solid and dashed curves for  $\text{Fe}^{2.5+}$  and  $\text{Fe}^{3+}$  were experimental  $f'$  values on XANES spectra of wustite ( $\text{FeO}$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ), respectively (Sasaki 1995). The  $\text{Fe}^{2.5+}$  curve was calculated by averaging the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  curves.

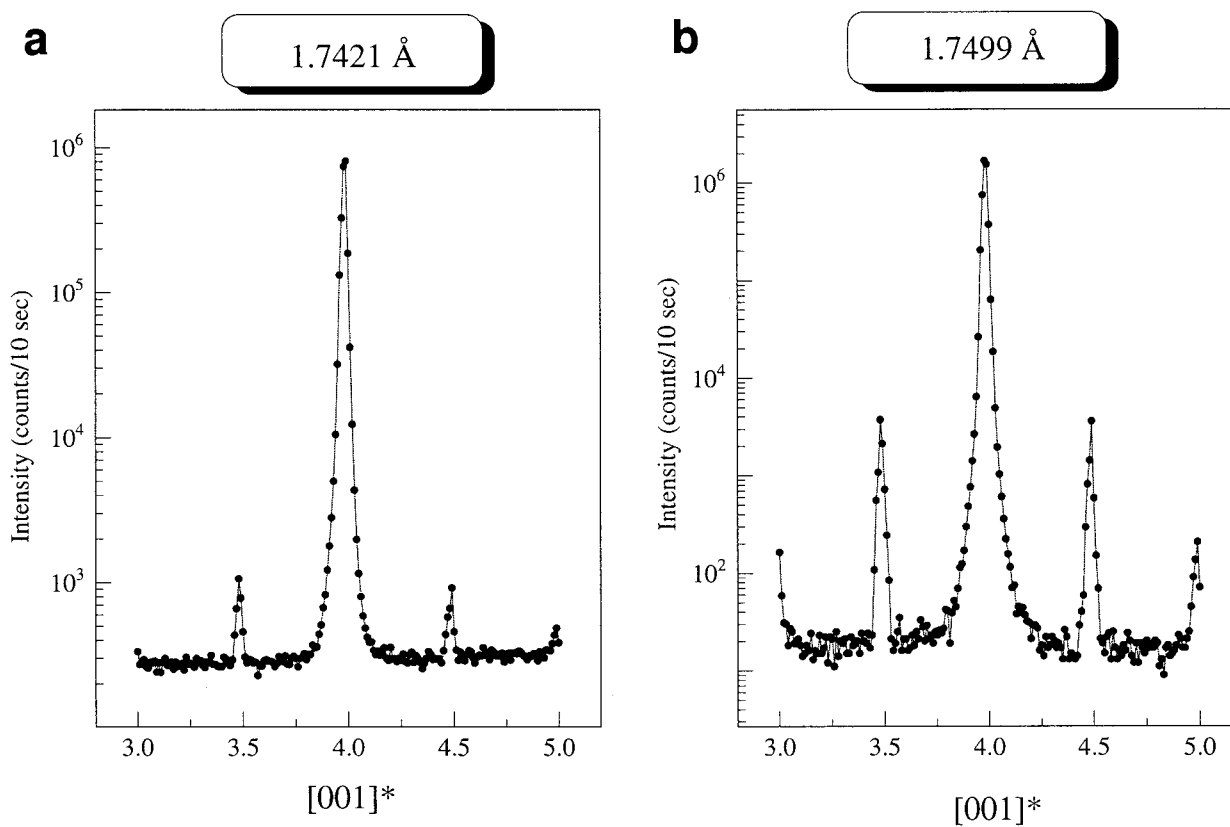
perature was calibrated using chromel-constantan thermocouple wires at the sample position. Integrated intensity data of low-temperature magnetite were collected for two crystals where each diffraction profile was step-scanned at intervals of  $0.02^\circ$  in  $\omega$ . The decrease in intensity of the incident beam was corrected with a standard 595 reflection. The energy-dependence experiments with intensity profiles were made for fundamental and superlattice reflections with an energy interval of 1 to 2 eV through the Fe  $K$  absorption edge.

### RESULTS AND DISCUSSION

#### Variation of structure factors between different ionic states

Magnetite,  $[\text{Fe}^{3+}]^A [\text{Fe}^{2+} \text{Fe}^{3+}]^B \text{O}_4$  has an inverse-spinel structure [cubic,  $Fd\bar{3}m$ ,  $a = 8.4000(3)$  Å] where A, B, and O are tetrahedral 8a, octahedral 16d, and oxygen 32e sites with atomic coordinates of  $(1/8, 1/8, 1/8)$ ,  $(1/2, 1/2, 1/2)$ , and  $(u, u, u)$  with  $u = 0.2555(2)$ , respectively (Sasaki 1997).

The validity for the VDC method was examined at room temperature using two types of reflections characteristic of the spinel structure. Figure 1 shows the energy dependence of observed structure factors for such reflections. The intensity for a 222-type reflection is mainly contributed by  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  of the B sites where the structure factor is written as  $F = 4 f^B \phi^B - 7.287 f^O \phi^O$  with the phase term  $\phi$  where the superscripts denote the atomic sites. The other is a 022 type, where the intensity contribution from the B sites is zero:  $F = -2 f^A \phi^A -$



**FIGURE 2.** Logarithmic intensity vs. the momentum transfer around the 044 reflection of magnetite measured at  $T = 102$  K. Superlattice reflections with half-integer indices clearly appear to have different intensities at wavelengths of (a)  $\lambda = 1.7421$  Å and (b)  $1.7499$  Å.

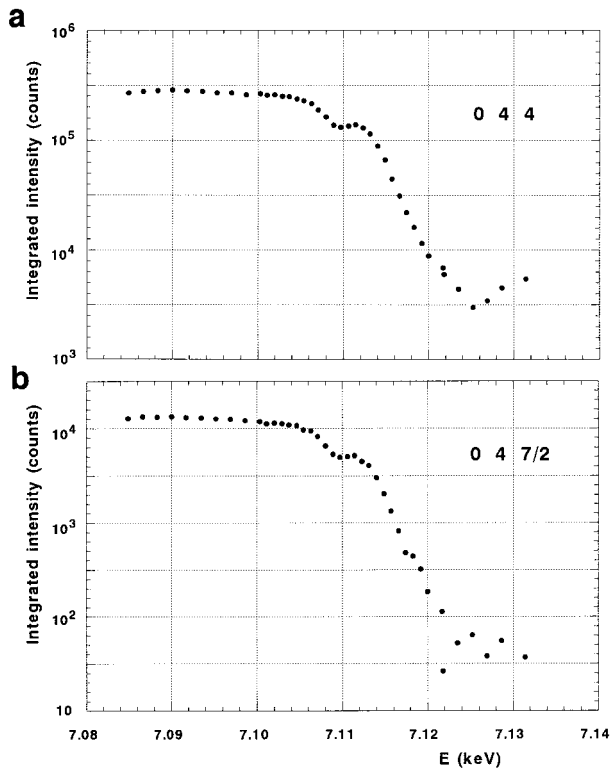
$0.032 f^{\circ} \phi^{\circ}$ . Here, the crystal structure factors measured at seven different wavelengths were normalized to observe the variation between the two-types of reflections. The normalization was that a difference in the structure factor for each reflection gives 0.0 at  $\lambda = 1.7551$  Å ( $E = 7.0643$  keV), where no difference exists between  $f'$  value of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

There is the difference in the X-ray energy between the two types of reflections. From curve fitting, the minima in the curves for the 222 and 226 reflections (Fig. 1) were estimated as 7.1226 and 7.1230 keV, respectively, giving an average of 7.1228 keV for the 222-type reflection. In contrast, the minima in the 026 and 246 curves are 7.1240 and 7.1236 keV, respectively, and the averaged energy for the 022-type reflection is 7.1238 keV ( $\lambda = 1.7404$  Å). The energy difference corresponding to the valence difference between the A and B sites was, therefore, approximately 1 eV. The ideal difference in the chemical shift would be 2.5 eV between  $\text{Fe}^{2.5+}$  in the B sites and  $\text{Fe}^{3+}$  in the A sites. The small deviation observed between the two sites may be due to the lower energy resolution of X-rays in intensity measurements at room temperature. Although the observed energy difference was relatively small, normalized structure factors of the B sites (open symbols) are always larger than those of

the A sites (solid symbols), suggesting Fe ions in the A sites are more ionic. The structure factors can be closely related to the experimental  $f'$  curves transformed by the integration algorithm of Cromer and Liberman (1975) from the XANES spectra (Fig. 1). Thus, the detection of valence difference for magnetite requires the VDC method.

#### Observation of superlattice reflections

Synchrotron X-ray profile measurements for single-crystals were made at wavelengths of  $\lambda = 0.7, 1.7421,$  and  $1.7499$  Å. Reflections with half-integer indices and reflections forbidden for the cubic phase were clearly observed at 102 K. Figure 2 shows the intensity profiles of superlattice reflections indexed as  $0\ 4\ \frac{1}{2}$  and  $0\ \bar{4}\ \frac{1}{2}$  (cubic cell). Appearance of extra reflections is consistent with previous observations and suggests the existence of a low- $T$  phase. The following characteristics in intensity distribution were coincident with neutron diffraction studies (Samuelson et al. 1968): strong  $0\ 4\ \frac{1}{2}$  and  $4\ 4\ \frac{1}{2}$  reflections, observable 104 reflection but undetected 401, and no intensity for  $0\ 0\ \frac{1}{2}$  and  $0\ 0\ \bar{1}\ \frac{1}{2}$ . Appearance of 300 and 500 reflections and extinction of 003 and 005 coincided with the previous X-ray studies (Yoshida and Iida 1977).

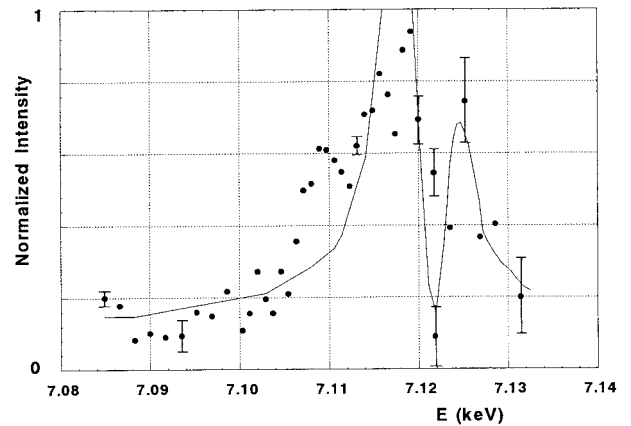


**FIGURE 3.** Variation of integrated intensities for the 044 and  $0\ 4\ \frac{1}{2}$  reflections at  $T = 102$  K. Each solid circle represents the integrated intensity with the measuring times at each  $\omega$ - $2\theta$  step of the intensity profile at an X-ray energy of 1 and 20 s, respectively.

The reflections of types  $0\ 4\ \frac{1}{2}$ ,  $0\ 4\ \frac{3}{2}$ ,  $0\ 4\ \frac{5}{2}$ ,  $4\ 4\ \frac{1}{2}$ ,  $4\ 4\ \frac{3}{2}$ , and  $4\ 4\ \frac{5}{2}$  gave the peak intensity ranging from 500 to 2000 cps. The existence of the reflections with half-integer indices requires a doubled cell. Further work is needed using the VDC method, although a monoclinic unit cell corresponding to  $\sqrt{2}a \times \sqrt{2}a \times 2a$  of the cubic spinel unit cell has been proposed with the space group  $Cc$  (Iizumi et al. 1982).

#### Energy dependence of superlattice reflections

Reflections with half-integer indices (Fig. 2) have a large difference in diffracted intensity for the two wavelengths  $\lambda = 1.7421$  Å [ $E = 7.1170$  keV;  $\Delta f' = f'(\text{Fe}^{2+}) - f'(\text{Fe}^{3+}) = -1.6$ ] and  $1.7499$  Å ( $E = 7.0853$  keV;  $\Delta f' = -0.18$ ). X-ray intensity measurements were performed at 102 K for low-temperature magnetite with various X-ray energies near the Fe *K* absorption edge. The energy dependence in diffracted intensity was examined using both fundamental and superlattice reflections. Figure 3 shows the variation of the integrated intensity for the 044 and  $0\ 4\ \frac{1}{2}$  reflections measured by the  $\omega$ - $2\theta$  step scans in the energy range from 7.0849 to 7.1218 keV. The dependence of intensity on energy for both reflections had characteristics related to an absorption profile at the Fe *K*-edge, with pre-edge structure at  $E = 7.11$  keV. The difference



**FIGURE 4.** Energy dependence of the diffracted intensity for the  $0\ 4\ \frac{1}{2}$  superlattice reflection near the Fe *K* absorption edge at  $T = 102$  K. The experimental errors for some intensity measurements are given by vertical bars. The solid curve is the calculation based on the difference between experimental values of  $f'(\text{Fe}^{2+})$  and  $f'(\text{Fe}^{3+})$ . The VDC effect of the pre-edge peak of the Fe *K*-edge may be observable near  $E = 7.11$  keV.

between the two curves is that the profile for the  $0\ 4\ \frac{1}{2}$  reflection in Figure 3b showed a fine structure of the intensity variation above  $E = 7.115$  keV.

The diffracted intensity of the  $0\ 4\ \frac{1}{2}$  reflection, where each intensity was corrected and normalized using the intensity variation of the 044 reflection, shows energy dependence (Fig. 4). The normalized intensity curve had two features that were larger than experimental errors. One is a positive peak around  $E = 7.11$  keV related to the pre-edge peak at the Fe *K*-edge. The characteristic pre-edge structure originated from the  $\text{Fe}^{3+}$  ions occupying the A sites (Matsumoto 1998). The other feature was a sharp minimum in the intensity distribution at  $E = 7.122$  keV. The existence of the minimum is not expected by averaging the  $f'$  values between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

The sharp minimum in intensity can be modeled using the  $f'$  difference between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  obtained from valence contrast in the calculation of scattering amplitude. The theoretical energy dependence (Fig. 4) was calculated based on the term  $[f'(\text{Fe}^{2+}) - f'(\text{Fe}^{3+})]^2$  with experimental  $f'$  values previously reported by Sasaki (1995). The observed was comparable with the calculated dependence on energy. The above calculation has a crystallographical meaning as follows: The low phase of magnetite has a double cell in the direction of the cubic  $a_3$  (or  $c$ ) axis as discussed earlier. Considered here is a simple case in which  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions occupy the atomic positions corresponding to the upper and lower halves of the double cell. Namely, the  $\text{Fe}^{2+}$  ions occurred at the atomic position  $(x, y, z)$  having the scattering power of  $f_0 + f'(\text{Fe}^{2+})$ , whereas the  $\text{Fe}^{3+}$  ions were at  $(x, y, z+1/2)$  having  $f_0 + f'(\text{Fe}^{3+})$ . The crystal structure factor for above case can be described as:

$$F = \{f_0 + f'(\text{Fe}^{2+})\}\phi(x, y, z) + \{f_0 + f'(\text{Fe}^{3+})\} \\ \times \phi(x, y, z + 1/2) \quad (1)$$

$$= \{f'(\text{Fe}^{2+}) - f'(\text{Fe}^{3+})\}\phi(x, y, z) + \{f_0 + f'(\text{Fe}^{3+})\} \\ \times \phi(x, y, z)[1 + \exp 2\pi i(l/2)] \quad (2)$$

where  $\phi(x, y, z) = \exp 2\pi i(hx + ky + lz)$  and the imaginary part of the atomic scattering factor is ignored. When the reflection index  $l$  is odd in the double cell, the second term of Equation 2 is zero because the second term in the square brackets is equal to  $-1$ . Under this condition, the structure factor is proportional to the difference,  $f'(\text{Fe}^{2+}) - f'(\text{Fe}^{3+})$ , which becomes zero if  $f'(\text{Fe}^{2+}) = f'(\text{Fe}^{3+})$  (Fig. 1). The reflection giving  $l = \text{odd}$  on the double cell corresponds to that with half-integer indices in the cubic cell such as  $0\ 4\ \frac{1}{2}$ .

Thus, it is strongly suggested that the superlattice peak contains the intensity component indicating charge difference between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , lowering of the crystal symmetry is accompanied by the lattice deformation and atomic rearrangements as indicated by existence of superlattice reflections at wavelengths away from the Fe  $K$ -edge. The VDC study shows directly that the charge ordering of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions occurs in magnetite below  $T_v$ .

#### ACKNOWLEDGMENTS

We thank H. Kawata, S. Todo, and K. Tsukimura for specimens and F. Saito and K. Yamawaki, T. Hanashima, and T. Mizobuchi for their experimental help. This study was performed under the auspices of the Photon Factory (PAC No. 97G169) and supported by JSPS-RFTF96P00205.

#### REFERENCES CITED

- Attfield, J.P. (1990) Determination of valence and cation distributions by resonant powder X-ray diffraction. *Nature*, 343, 46–49.
- Bearden, J.A. and Burr, A.F. (1989) Reevaluation of X-ray atomic energy levels. *Reviews of Modern Physics*, 39, 125–142.
- Chiba, K., Suzuki, K., and Chikazumi, S. (1975). Diffuse electron scattering from magnetite above the Verwey transition temperature. *Journal of Physical Society of Japan*, 39, 839–840.
- Cromer, D.T. and Liberman, D. (1970) Relativistic calculation of anomalous scattering factors for X-rays. *Journal of Chemical Physics*, 53, 1891–1898.
- Gao, Y., Frost-Jensen, A., Pressprich, M.R., and Coppens, P. (1992) Valence contrast by synchrotron resonance scattering: application to a mixed-valence manganese compound, *Journal of American Chemical Society*, 114, 9214–9215.
- Gao, Y., Pressprich, M.R., and Coppens, P. (1993) Anomalous-scattering contrast study of the mixed-valence charge-density-wave conductor  $\text{NbSe}_3$ . *Acta Crystallographica*, A49, 216–219.
- Iizumi, M., Koetzle, T.F., Shirane, G., Chikazumi, S., Matsui, M., and Todo, S. (1982) Structure of magnetite ( $\text{Fe}_3\text{O}_4$ ) below the Verwey transition temperature. *Acta Crystallographica* B38, 2121–2133.
- Kwei, G.H., von Dreele, R.B., Williams, A., Goldstone, J.A., Lawson, A.C. II, and Warburton, W.K. (1990) Structure and valence from complementary anomalous X-ray and neutron powder diffraction. *Journal of Molecular Structure*, 223, 383–406.
- Matsumoto, K. (1998) Electronic and magnetic structures of transition-metal ferrites investigated with the X-rays at the Fe  $K$ -edge, Master's of Science Thesis, Tokyo Institute of Technology.
- Samuelsen, J., Bleeker, E.J., Dobrzynski, L., and Riste, T. (1968) Neutron scattering from magnetite below 119 K. *Journal of Applied Physics*, 39, 1114–1115.
- Sasaki, S. (1995)  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions distinguishable by X-ray anomalous scattering: Method and its application to magnetite. *Review of Scientific Instrumentation*, 66, 1573–1576.
- (1997) Radial distribution of electron density in magnetite,  $\text{Fe}_3\text{O}_4$ . *Acta Crystallographica* B, 53, 762–766.
- Sasaki, S., Toyoda, T., Yamawaki, K., and Ohkubo, K. (1998) Valence-difference contrast measurements utilizing X-ray anomalous scattering. *Journal of Synchrotron Radiation*, 5, 920–922.
- Shapiro, S.M., Iizumi, M., and Shirane, G. (1976) Neutron scattering study of the diffuse critical scattering associated with the Verwey transition in magnetite ( $\text{Fe}_3\text{O}_4$ ). *Physical Review* B14, 200–207.
- Toyoda, T., Sasaki, S., and Tanaka, M. (1997) X-ray diffuse scattering study of magnetite by the valence-difference contrast method. *Japanese Journal of Applied Physics*, 36, 2247–2252.
- Verwey, E.J.W., Haayman, P.W., and Romeijn, F.C. (1947) Physical properties and cation arrangement of oxides with spinel structures: II electronic conductivity. *Journal of Chemical Physics*, 15, 181–187.
- Warner, J.K., Cheetham, A.K., Cox, D.E., and von Dreele, R.B. (1992) Valence contrast between iron sites in a  $\text{Fe}_2\text{O}_3$ : a comparative study by magnetic neutron and resonant X-ray powder diffraction. *Journal of American Chemical Society*, 114, 6074–6080.
- Wilkinson, A.P., Cheetham, A.K., and Cox, D.E. (1991) Study of oxidation-state contrast in gallium dichloride by synchrotron X-ray anomalous scattering. *Acta Crystallographica* B47, 155–161.
- Yamada, T., Suzuki, K., and Chikazumi, S. (1968) Electron microscopy of orthorhombic phase in magnetite. *Applied Physics Letters*, 13, 172–174.
- Yamada, Y., Mori, M., Noda, Y., and Iizumi, M. (1979) Neutron diffuse scattering in  $\text{Fe}_3\text{O}_4$  due to molecular polarons. *Solid State Communications*, 32, 827–830.
- Yoshida, J. and Iida S. (1977) X-ray diffraction study on the low temperature phase of magnetite. *Journal of Physical Society of Japan*, 42, 230–237.

MANUSCRIPT RECEIVED JUNE 9, 1998

MANUSCRIPT ACCEPTED SEPTEMBER 29, 1998

PAPER HANDLED BY JOHN PARISE