

# Cation Distribution of $\text{ZnFe}_2\text{O}_4$ and $\text{CoFe}_2\text{O}_4$ Spinel From Anomalous X-Ray Scattering

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The distribution of  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  cations in ferrite spinels has been determined by applying anomalous X-ray scattering (AXS) near the  $K$  absorption edges of Fe, Co and Zn. The energy dependence of the reflection intensities of  $\text{ZnFe}_2\text{O}_4$ , detected at the Fe  $K$  and Zn  $K$  absorption edges, can only be explained when all  $\text{Zn}^{2+}$  being allocated to the tetrahedral site formed by oxygens. On the other hand, the results for  $\text{CoFe}_2\text{O}_4$  suggest that 78% of  $\text{Co}^{2+}$  occupy the octahedral site, and that the present  $\text{CoFe}_2\text{O}_4$  sample is classified as *inverse* spinel, although a partial disorder is included. The usefulness of this AXS method coupled with the common Rietveld analysis was well-recognized by determining the cation distribution even in a system with next neighboring elements of the periodic table.

**Key words:** Anomalous X-ray scattering, Rietveld, Synchrotron radiation, Ferrite, Spinel,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ .

## I. Introduction

Ferrite spinels are expressed by the general formula of  $\text{MFe}_2\text{O}_4$ , where M is a divalent cation. The unit cell contains eight formula units and is usually referred to space group  $Fd3m$  ( $O_h^7$ ) with cations occupying special positions of  $8a$  and  $16d$ . The ideal structure consists of a cubic close packing of oxygens (32e), in which one-eighth of the tetrahedral and half of the octahedral interstices are occupied. For example,  $\text{Zn}^{2+}$  cations usually prefer to occupy the tetrahedral sites in  $\text{ZnFe}_2\text{O}_4$  as a “normal” spinel. On the other hand, many ferrites have an “inverse” or “partly inverse” structure, where the divalent  $\text{M}^{2+}$  cations are distributed both in the octahedral and tetrahedral sites. Since the magnetic properties of ferrite spinels are sensitive to the cation distribution, it is of great importance to determine their degree of inversion [1]. The determination of the cation distribution in ferrites by the usual X-ray diffraction method is generally not easy because the X-ray scattering ability of the component M, such as Zn and Ni, is close to that of host element Fe. Anomalous X-ray scattering (hereafter referred to as AXS) at energies near the absorption edge of Fe and M is one way to bring about a significant

breakthrough in this difficulty by permitting an appreciable difference in the crystallographic structure factors [2–4].

The X-ray scattering amplitude  $f$  is known to consist of a photon-energy independent term  $f^0$  and the energy dependent real  $f'(E)$  and imaginary  $f''(E)$  terms, referred to as anomalous scattering factors:

$$f(Q, E) = f^0(Q) + f'(E) + if''(E), \quad (1)$$

where  $Q$  is the value of the wave vector and  $E$  is the energy of the incident X-rays. The terms  $f'(E)$  and  $f''(E)$  are usually small because X-ray interact weakly with the substances of interest. The change in these terms, however, indicates a significant energy dependence when the energy of the incident X-rays is close to the absorption edge of the constituents. Thus, such energy-dependence of the X-ray scattering factor induces a variation in intensity, and the detected changes enable the study of the fine structure or electronic states of various materials. This is strongly supported by making available the intense white radiation (continuous energy spectrum) from a synchrotron radiation source and thus enabling the use of an energy in which the AXS is the greatest. It is worth mentioning for the AXS that the characteristic absorption edge of any element is separated, at least by several hundred eV, so that a sufficient atomic sensitivity could be obtained even for substances containing next neighbor elements in the periodic table.

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The main purpose of this work is to determine the cation distribution in  $\text{ZnFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  spinels using the AXS method at the  $K$  absorption edges of Fe, Co, and Zn coupled with common Rietveld analysis.

## II. Fundamentals of Structural Analysis Using the AXS Method

Theoretical values  $f'(E)$  and  $f''(E)$  for Fe, Co and Zn are plotted in Fig. 1 as functions of energy, as calculated by using Cromer-Liberman's relativistic scheme for an isolate atom [4, 5]. The incident energies, employed in the present AXS measurements, are indicated with vertical broken lines. It may be worth mentioning that the agreement between the experimental and theoretical values of the anomalous scattering factors is well confirmed at the lower energy side of the absorption edge. This is one of the reasons for selecting these incident energies.

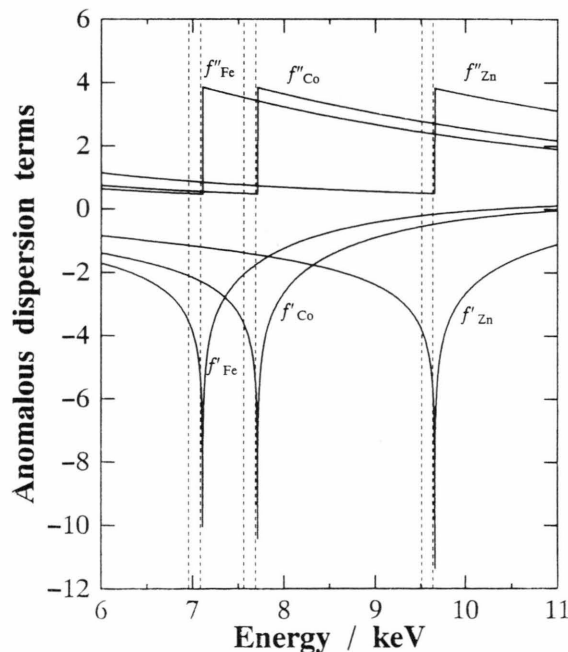


Fig. 1 Energy dependence of the anomalous dispersion factors  $f'(E)$  and  $f''(E)$  for Fe, Co and Zn in the close vicinity of their respective  $K$  absorption edges of 7.111, 7.710, and 9.660 keV. The incident energies used in the present AXS measurements are indicated by the vertical dashed lines.

The diffracted intensity of the  $hkl$  reflection from a crystalline powder in reflection geometry may be expressed as

$$I_{hkl}(E) = K p I_0(E) \lambda^3 P L A \frac{|F_{hkl}(E)|^2}{v_c^2}, \quad (2)$$

where

- $I_{hkl}$ : integrated intensity,
- $\lambda$ : wavelength,
- $I_0$ : incident intensity,
- $p$ : multiplicity factor,
- $P$ : polarization factor,
- $L$ : Lorentz factor,
- $A$ : absorption factor,
- $F_{hkl}$ : structure factor for the unit cell,
- $v_c$ : volume of unit cell,
- $K$ : scale factor.

The quantity  $F_{hkl}$  is given by using three terms for  $8a$ ,  $16d$  and  $32e$  sites:

$$\begin{aligned} F_{hkl} = & f_{\text{tet}} \exp[B_{\text{tet}}(\sin \theta/\lambda)^2] \sum_{8a} \exp[2\pi i(hx + ky + lz)] \\ & + f_{\text{oct}} \exp[B_{\text{oct}}(\sin \theta/\lambda)^2] \\ & \cdot \sum_{16d} \exp[2\pi i(hx + ky + lz)] \\ & + f_{\text{oxygen}} \exp[B_{\text{oxygen}}(\sin \theta/\lambda)^2] \\ & \cdot \sum_{32e} \exp[2\pi i(hx + ky + lz)], \end{aligned} \quad (3)$$

where  $(x, y, z)$  are the fractional coordinates.  $B_{\text{tet}}$ ,  $B_{\text{oct}}$  and  $B_{\text{oxygen}}$  are the isotropic temperature factors for the tetrahedral site, octahedral site and site for oxygen, respectively. The summation extends over all atoms in the unit cell.

Let us introduce the degree of inversion  $x$ , defined by the fraction of  $\text{Fe}^{3+}$  cations in the tetrahedral sites. The scattering factors  $f_{\text{tet}}$  and  $f_{\text{oct}}$  are given as functions of  $x$  as follows:

$$\begin{aligned} f_{\text{tet}} &= (1-x)f_{\text{M}} + x f_{\text{Fe}}, \\ f_{\text{oct}} &= \frac{x}{2} f_{\text{M}} + \frac{2-x}{2} f_{\text{Fe}}. \end{aligned} \quad (4)$$

It should be noted that  $x=0.0$  and  $x=1.0$  correspond to the cation distribution of all cations occupying the tetrahedral site and the octahedral site, respectively.

When the intensities are measured at two energies  $E_1$  and  $E_2$  in the close vicinity of the absorption edge of a specific element, the following simple but useful

relation can readily be obtained [6]:

$$r_{hkl,exp} = \frac{I_{hkl}(E_1)/(\lambda_{E_1}^3 P_{E_1} L_{E_1} A_{E_1})}{I_{hkl}(E_2)/(\lambda_{E_2}^3 P_{E_2} L_{E_2} A_{E_2})} \frac{I_0(E_2)}{I_0(E_1)} \\ = \frac{|F_{hkl}(E_1)|^2}{|F_{hkl}(E_2)|^2} \quad (5)$$

The detected variation in intensity with energy is attributed to the anomalous scattering terms of a specific element, since the anomalous dispersion effects arising from the other elements appear to be insignificant in this energy region. Thus, by comparing the measured  $r_{hkl,exp}$  at two energies close to the edge with the values of  $r_{hkl,cal}$  calculated from the model cation distribution in the usual manner, the cation distribution can be quantitatively determined. In data processing, the iterative procedure displayed in Fig. 2 and the following  $R$ -factor are introduced to obtain a significant solution:

$$R_{AXS} = \sum_{hkl} \frac{[r_{hkl,exp} - r_{hkl,cal}]^2}{\sigma_{hkl,exp}} \quad (6)$$

$\sigma_{hkl,exp}$  is a fractional weight of  $(1 - r_{hkl,exp})^{-2}$ . The cation distribution of the present ferrite spinel samples can be determined so as to minimize the factor  $R_{AXS}$  of AXS measurements at energies close to the absorption edges of M and Fe.

### III. Experimental

The AXS measurements were carried out at a beam line (6B station) of synchrotron radiation in the Photon Factory, National Laboratory for High Energy Physics, Tsukuba, Japan. The details of the experimental set-up and data processing for the AXS measurements have been described in [6]. Only some necessary additional points are given below.

The sample was mounted on a double-axis goniometer placed vertically to eliminate the polarization effect. The incident X-ray beam was monitored by an N<sub>2</sub> gas flow type ion chamber placed in front of the sample. The scattering intensity was measured at each angle for certain preset counts of this ion chamber, so as to keep constant the total number of photons incident on the sample. The incident energies used in the present AXS measurements are a pair of 6.961 keV and 7.086 keV, which corresponds to 150 and 25 eV below the Fe K absorption edge (7.111 keV). Similarly, we employed two pairs of incident energies 7.560 keV/7.684 keV and 9.511 keV/9.636 keV below the Co K absorption edge (7.710 keV) and Zn K absorption edge (9.660 keV), respectively. These energies were tuned by using a Si(111) double-crystal monochromator. Its optimum energy resolution is about 5 eV at 10 keV [7]. The effect of the higher harmonics of the 333 reflection was reduced by intentionally detuning the second Si crystal monochromator with a piezo electric device, although about one fifth of the intensity of the first-order diffraction was lost.

In the spinel-type structure, the intensity ratio of 422 reflection at two energies provides the structural information only on the cations in the tetrahedral site, whereas the ratio of 222 reflection can be attributed to that of the octahedral site. On the other hand, the ratio of 440 reflection was necessary so as to estimate the  $I_0(E_1)/I_0(E_2)$  in (5), because the intensity of 440 reflection is known to be independent of the cation distribution in the present spinel structure. Therefore, the intensity ratios of 222, 422, and 440 reflections were subject to the present AXS measurements at energies close to the absorption edges of Fe, Co, and Zn, and this made the valuable and limited beam time of a synchrotron radiation source effective [8].

### IV. Results and Discussion

A ZnFe<sub>2</sub>O<sub>4</sub> sample was prepared from commercial zinc-ferrite powder of 99.9 mass% purity (Kojundo

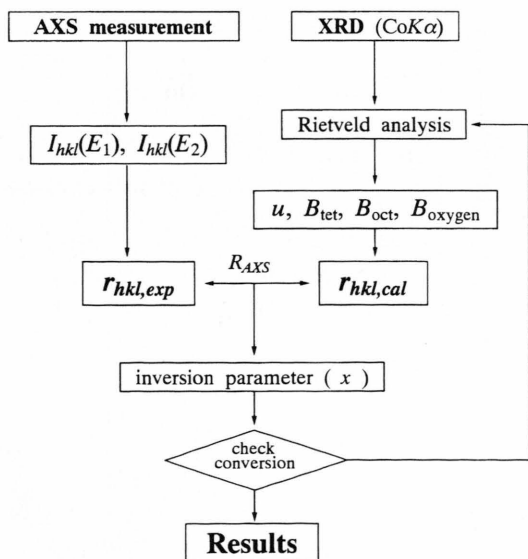


Fig. 2. Flow-chart of the iterative procedure used in the present study for obtaining improved X-ray structural information from the AXS measurements coupled with common Rietveld analysis.

Chemical Laboratory Co., Ltd.) by heating at 773 K for 72 hours in air, and quenched to room temperature [9]. On the other hand, a  $\text{CoFe}_2\text{O}_4$  sample was prepared as follows. Solutions of 0.05 mol of  $\text{Fe}_2(\text{SO}_4)_3 \cdot 13\text{H}_2\text{O}$  and  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  were mixed with a solution containing 1.55 mole NaOH and aged at 398 K for 8 hours. The resultant precipitate was freeze-dried after applying a centrifugal separator several times, and subsequently powdered samples by heating at 1073 K for 60 hours in air.

The diffraction patterns for common Rietveld analysis [10] were obtained by using  $\text{Co K}\alpha$  radiation with a pyrolytic graphite monochromator in a diffracted beam. Data were collected over the range  $2\theta = 17$  to  $140^\circ$ . X-ray diffraction patterns of two samples agreed well with the compiled JCPDS data of No. 22–1021 ( $\text{ZnFe}_2\text{O}_4$ ) and No. 22–1086 ( $\text{CoFe}_2\text{O}_4$ ). The crystal structures were refined by Rietveld analysis with a generalized computer package program PFLS [11] within the constraints of chemical formula and full site occupancy. For calculation of the structure factors, the atomic scattering factors for  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  [12] and  $\text{O}^{2-}$  [13] were used together with dispersion corrections [4, 5]. It may be stressed here that the lattice constant was determined by the whole powder pattern decomposition method with an internal standard of NBS Si(640b) [14].

The values of the lattice constant  $a$ , the structural parameters  $u$  (commonly known as the positional parameter of oxygen), and  $B$  determined by the Rietveld analysis are given in Table 1, together with the final values of  $R_{\text{Bragg}}$  and  $R_F$  [11]. The resultant profile of the Rietveld analysis for the  $\text{CoFe}_2\text{O}_4$  sample is shown in Fig. 3, as an example. Figure 4 shows the energy dependence of two reflection peak intensities of  $\text{ZnFe}_2\text{O}_4$  obtained from the AXS measurements with two energies at the absorption edges of Fe and Zn. A significant intensity variation is detected in the 222 reflection at the Fe K absorption edge, while not in the 422 reflection. On the other hand, the reverse behavior was clearly detected in the AXS results at the Zn K absorption edge. This strongly supports that the present  $\text{ZnFe}_2\text{O}_4$  sample is of the normal type, where the  $\text{Zn}^{2+}$  cations are quite likely ordered in the tetrahedral site, and the  $\text{Fe}^{3+}$  cations are octahedrally coordinated.

The anomalous dispersion effects of Fe and Zn on the intensity ratio at two energies can readily be calculated as functions of the degree of inversion  $x$ . The results of  $x$ , which give the minimum value of  $R_{\text{AXS}}$  in

Table 1. The crystal structure refinement of  $\text{ZnFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  spinels, using the Rietveld and AXS methods.

	$a$ (nm)	$x$	$u$	$B_{\text{tet}}$ (nm <sup>2</sup> )	$B_{\text{oct}}$ (nm <sup>2</sup> )	$B_{\text{oxygen}}$ (nm <sup>2</sup> )	$R_{\text{Bragg}}$ (%)	$R_F$ (%)
$\text{ZnFe}_2\text{O}_4$	0.8442	0.00	0.2612	0.0071	0.0044	0.0078	2.96	2.28
$\text{CoFe}_2\text{O}_4$	0.8393	0.78	0.2560	0.0056	0.0071	0.0119	3.24	2.67

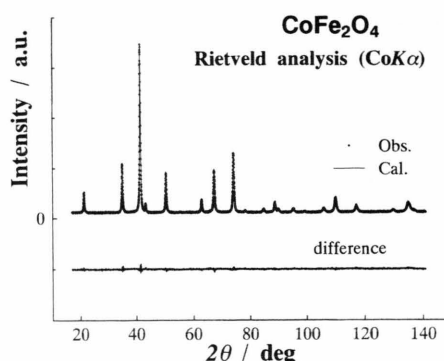


Fig. 3. X-ray diffraction patterns of  $\text{CoFe}_2\text{O}_4$ . Top: the calculated profile is compared with the observed values indicated by crosses. Bottom: plot of the difference between the two.

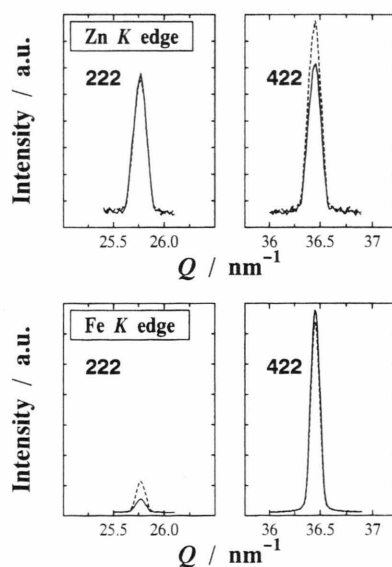


Fig. 4. The diffraction peak intensities of  $\text{ZnFe}_2\text{O}_4$  measured with two energies at the absorption edge of Fe and Zn. Fe K edge: solid (7.086 keV), dashed (6.961 keV), Zn K edge: solid (9.636 keV), dashed (9.511 keV).

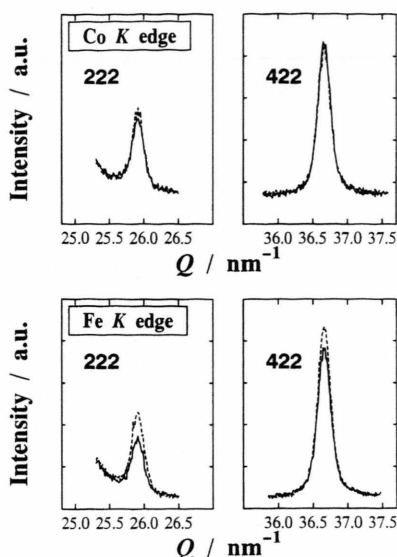


Fig. 5. The diffraction peak intensities of  $\text{CoFe}_2\text{O}_4$  measured with two energies at the absorption edge of Fe and Co. Fe K edge: solid (7.086 keV), dashed (6.961 keV), Co K edge: solid (7.684 keV), dashed (7.560 keV).

Table 2. The values of  $r_{hkl, \text{exp}}$  obtained by the present AXS measurements,  $r_{hkl, \text{cal}}$  calculated from the model cation distribution and the resultant inversion parameter  $x$  for  $\text{ZnFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$ .

		$\text{ZnFe}_2\text{O}_4$		$\text{CoFe}_2\text{O}_4$	
	Reflection	$r_{hkl, \text{exp}}$	$r_{hkl, \text{cal}}$	$r_{hkl, \text{exp}}$	$r_{hkl, \text{cal}}$
Fe AXS	422	1.02	1.00	0.83	0.83
	222	0.40	0.41	0.66	0.67
Co AXS	422			0.98	0.98
	222			0.88	0.86
Zn AXS	422	0.76	0.79		
	222	1.02	1.01		
inversion parameter $x$		0.00		0.78	

(6), are listed in Table 2 together with the values of  $r_{hkl, \text{exp}}$  and  $r_{hkl, \text{cal}}$ . These facts quantitatively confirm that all  $\text{Zn}^{2+}$  cations occupy the tetrahedral site in the  $\text{ZnFe}_2\text{O}_4$  sample presently investigated. For convenience, the numerical values of  $f'(E)$  and  $f''(E)$  used in this calculation are summarized in Table 3.

A similar structural analysis has been made for the  $\text{CoFe}_2\text{O}_4$  sample. Figure 5 shows the energy dependence of two reflection peak intensities of  $\text{CoFe}_2\text{O}_4$  obtained from the AXS measurements with two energies at the K absorption edges of Fe and Co. The intensity variation with energy is, more or less, detected in all cases measured at the Fe and Co K edges. This implies a disordered distribution of Co and Fe cations between the tetrahedral and octahedral sites. The measured intensity ratio can be well-reproduced only when using the inversion parameter of  $x=0.78$ , as shown in Table 2. This corresponds to the condition that the variation of the  $R_{\text{AXS}}$  factor indicates its minimum value. Thus, it may be safely concluded that almost one-fourth of the tetrahedral sites are occupied by  $\text{Co}^{2+}$  cations. To our best knowledge this is the first quantitative information of the cation distribution of  $\text{Co}^{2+}$  cations in  $\text{CoFe}_2\text{O}_4$  by X-ray diffraction technique. According to the discussion given by O'Neill and Navrotsky [15], the lattice constant of  $a=0.838$  nm and the oxygen parameter of  $u=0.255$  can be estimated when the inversion parameter is equal to 0.78. These values agree surprisingly well with the present results of Table 1. However, the lattice constant of ferrite samples is known to rely frequently upon sample preparation, and the variation of cation distribution with heat treatment is also suggested from magnetic property measurements of  $\text{CoFe}_2\text{O}_4$  [16]. Such points should be answered by making available systematic structural information from AXS mea-

Table 3. Anomalous dispersion terms  $f'$  and  $f''$  used in this work.

	Energy/keV	$f'_{\text{Fe}}$	$f''_{\text{Fe}}$	$f'_{\text{Co}}$	$f''_{\text{Co}}$	$f'_{\text{Zn}}$	$f''_{\text{Zn}}$	$f'_{\text{O}}$	$f''_{\text{O}}$
Fe AXS	6.961	-3.50	0.49	-2.10	0.57	0.21	2.44	0.06	0.04
	7.086	-5.09	0.47	-2.26	0.55	0.17	2.39	0.06	0.04
Co AXS	7.560	-2.07	3.53	-3.59	0.49			0.05	0.04
	7.684	-1.78	3.45	-5.24	0.48			0.05	0.04
Zn AXS	9.511	-0.21	2.44			3.80	0.50	0.03	0.02
	9.636	-0.17	2.38			5.68	0.49	0.03	0.02
Co K $\alpha$	8.048	-3.37	0.49	-2.07	0.57	-1.14	0.89	0.06	0.04



surements on sample prepared by various synthetic methods as a function of temperature or oxygen fugacity.

In conclusion, the present improved structural analysis using the X-ray anomalous scattering (AXS) coupled with Rietveld analysis clearly reveals the overall tetrahedral preference of  $\text{Zn}^{2+}$  cations in the present  $\text{ZnFe}_2\text{O}_4$  sample and provides the first quantitative information on the cation distribution in  $\text{CoFe}_2\text{O}_4$ . Next neighboring elements in the periodic table cannot be distinguished with the conventional X-ray diffraction method. However, the AXS method can bring about a significant breakthrough in this difficulty, as it has been demonstrated in this work

using the results of  $\text{CoFe}_2\text{O}_4$ . It would be very interesting to extend the AXS method to other spinel-type materials in order to see clearer the dependence of the characteristic properties of spinels on their atomic scale structure.

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