Crystal-site-selective spectrum of Fe_3O_4 obtained by synchrotron Mössbauer diffraction

^{57}Fe Mössbauer spectroscopy is a local and dynamic probe that is very useful for investigating iron compounds. Through the hyperfine structure obtained by analysis of the spectrum, such as the isomer shift, quadrupole splitting, and hyperfine field, we can examine the electronic state, local crystal structure, and magnetic structure of Fe. In many cases, materials contain several Fe-sites, and their Mössbauer spectra are composed of the superposition of the corresponding subspectra. As a result, it often becomes difficult to analyze the spectrum and to determine precise hyperfine parameters. On the other hand, diffraction measurements, such as X-ray and neutron diffraction, provide information on each crystallographic site because their intensities are given by the structure factors of constituent atoms. The combination of both techniques, i.e., Mössbauer diffraction, enables us to obtain a crystal-site-selective spectrum.

The synchrotron Mössbauer source at SPring-8 **BL11XU**, where the ^{57}Fe energy domain spectrum is directly obtained, is very suitable for studying Mössbauer diffraction. The γ-ray (π-polarized, wavelength 0.8603 Å) emitted from the ^{57}FeBO$_3$ nuclear Bragg monochromator has high directivity (angular divergence 3.0″) and extremely high brilliance (10^5 times that of a usual radioactive source). Recently, using this source, we have developed a Mössbauer diffractometer by installing a $\theta-2\theta$ goniometer as a sample stage between the nuclear monochromator and a detector [1,2]. A crystal-site-selective spectrum can be obtained by using only a selected γ-ray reflection, which enables us to determine precise hyperfine parameters in multi-Fe-site compounds. There still remains a problem that the reflected γ-ray from a specimen consists of the γ-ray scattered by the nuclei after the resonance (nuclear resonant scattering) and that scattered by the electrons of the atoms (electron scattering). The former gives a crystal-site-selective emission spectrum, while the latter only gives a usual transmission spectrum regardless of the reflection index. Therefore, in order to obtain a site-selective Mössbauer spectrum, only the nuclear resonant scattering should be extracted, or the electron scattering should be suppressed. For this purpose, we propose three methods:

(a) *Use of a pure nuclear Bragg reflection (pure nuclear method)*

When the Fe magnetic structure has a lower symmetry than the crystal symmetry, the pure nuclear Bragg reflection can be obtained, where the electron scattering is completely suppressed. A typical example is a forbidden reflection of a collinear antiferromagnet.

(b) *Use of a reflection having a Bragg angle (θ_B) near 45° (45° method)*

This method utilizes the nature of a π-polarized γ-ray where the polarization factor of the electron scattering $P_e = \cos 2\theta_B$ vanishes when $\theta_B = 45°$.

(c) *Use of a reflection from a polarization analyzer (polarization analyzer method)*

This method is essentially the same as the 45° method, except that an extra diffraction at a polarization analyzer, installed between the sample and the detector, is used. As an analyzer crystal, the Si(840) plane ($\theta_B = 45.1°$) is suitable. The analyzer cuts off the electron scattering (π-polarization) regardless of the reflection index of the sample.

In the present research, we applied the 45° method to a typical multi-Fe-site compound, magnetite (Fe_3O_4) [3]. Magnetite has a cubic inverse-spinel structure (space group $Fd\bar{3}m$, lattice constant a = 8.396 Å at room temperature). The crystal structure is shown in Fig. 1. The A-site (8a, site symmetry $\bar{4}3m$) is occupied by an Fe^{3+} ion, while the B-site (16d, site symmetry $\bar{3}m$) is occupied by equal numbers of Fe^{2+} and Fe^{3+} ions. A schematic view of the experimental setup is illustrated in Fig. 2. A single-crystal specimen of 95% enriched $^{57}Fe_3O_4$ fabricated by the floating zone melting method (FZ) in a controlled oxygen pressure was mounted on a goniometer. The reflected γ-rays with 666 (θ_B = 32.26°) and 10 10 0 (θ_B = 46.48°) reflections were used to collect the spectra at room temperature with measurement times of 6 and 18 h, respectively. The Fe nuclear structure factors of the
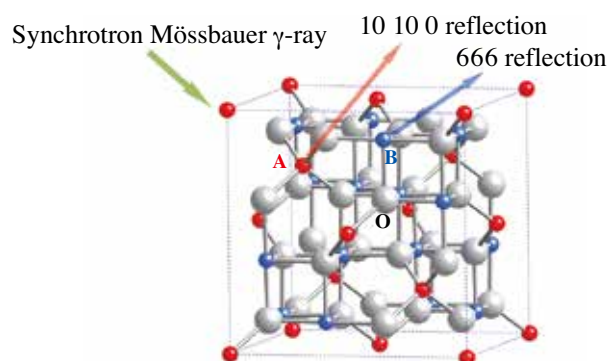

Fig. 1. Crystal structure of Fe_3O_4. A, B, and O denote A-site Fe, B-site Fe, and oxygen, respectively. The diffraction image for the 666 and 10 10 0 reflections is also illustrated.

666 and 10 10 0 reflections consist of only B-site and A-site Fe, respectively. The diffraction image is also illustrated in Fig. 1.

The Mössbauer diffraction spectrum collected by using only the 666 and 10 10 0 reflected γ-ray is shown in Figs. 3(a) and 3(b), respectively. The 666 reflection spectrum is mainly composed of the B-site emission spectrum due to the nuclear resonant scattering. However, there are some small dips due to the electron scattering since P_e is not zero but 0.43 for this reflection. The interference effect between the nuclear resonant scattering and the electron scattering, i.e., broadening of the lines, asymmetric line shapes, and a slope of the base line, is also notable. In such a case, the spectral shape can be expressed by the Fano function. We successfully analyzed the spectrum as shown by the smooth red curve in the figure. The assignments B(n), A(e), and B(e) denote the B-site spectrum due to the nuclear resonant scattering and the A- and B-site spectra due to the electron scattering, respectively. On the other hand, the 10 10 0 reflection spectrum is only composed of the A-site emission spectrum due to the nuclear resonant scattering and there is no interference effect ($P_e = -0.05$). As a first-order approximation, the spectrum can be analyzed by the Lorentzian function as shown by the smooth red curve in the figure.

Note here that we also succeeded in obtaining the crystal-site-selective spectrum by using the other two methods (a) and (c) [4,5]. For the pure nuclear method, another typical multi-Fe-site compound, the collinear antiferromagnet Fe_3BO_6, was used. Well-resolved 300, 500, and 700 reflection spectra were quantitatively analyzed using a formula based on the dynamical theory of diffraction. The intensity ratio of Fe1 to Fe2 subspectra originating from two different Fe sites in Fe_3BO_6 was in accordance with the nuclear

structure factor. For the polarization analyzer method, the 222 reflection of Fe_3O_4 was used and only the B-site emission spectrum was obtained. Synchrotron Mössbauer diffraction is a clearly powerful tool for analyzing the highly complex Mössbauer spectrum in multisite materials.
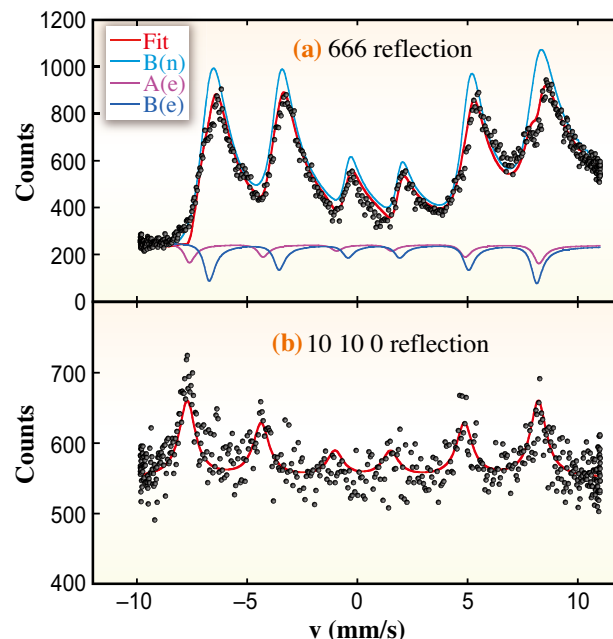

Fig. 3. Mössbauer diffraction spectrum of $^{57}Fe_3O_4$ collected by using (a) 666 and (b) 10 10 0 reflected γ-ray at room temperature. The assignments B(n), A(e), and B(e) denote the B-site spectrum due to the nuclear resonant scattering and the A- and B-site spectra due to the electron scattering, respectively.
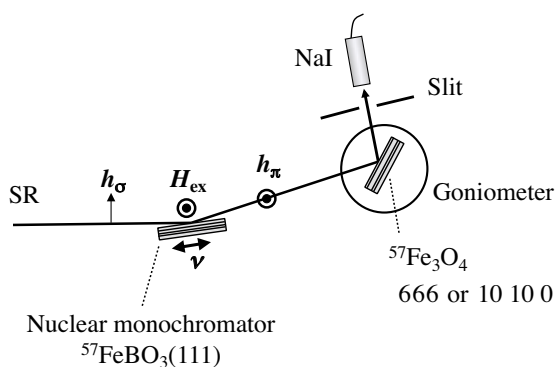

Fig. 2. Schematic view of the experimental setup at BL11XU. SR: synchrotron radiation. h_σ and h_π: unit magnetic field vectors of the incident (σ-polarized) and diffracted (π-polarized) radiation at the $^{57}FeBO_3$ nuclear monochromator, respectively. H_{ex}: external field (150 Oe) applied to the nuclear monochromator. NaI: scintillation detector.

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