Application of focused-beam flat-sample method to synchrotron powder X-ray diffraction with anomalous scattering effect

M Tanaka¹, Y Katsuya¹ and Y Matsushita²

¹ Synchrotron X-ray Station at SPring-8, National Institute for Materials Science, Sayo, Hyogo, Japan
² Materials Analysis Station, National Institutes for Materials Science, Tsukuba, Ibaraki, Japan

E-mail: masahiko@spring8.or.jp

Abstract. The focused-beam flat-sample method (FFM), which is a method for high-resolution and rapid synchrotron X-ray powder diffraction measurements by combination of beam focusing optics, a flat shape sample and an area detector, was applied for diffraction experiments with anomalous scattering effect. The advantages of FFM for anomalous diffraction were absorption correction without approximation, rapid data collection by an area detector and good signal-to-noise ratio data by focusing optics. In the X-ray diffraction experiments of CoFe₂O₄ and Fe₃O₄ (By FFM) using X-rays near the Fe K absorption edge, the anomalous scattering effect between Fe/Co or Fe²⁺/Fe³⁺ can be clearly detected, due to the change of diffraction intensity. The change of observed diffraction intensity as the incident X-ray energy was consistent with the calculation. The FFM is expected to be a method for anomalous powder diffraction.

1. Introduction

The focused-beam flat-sample method (FFM), which is a method for high-resolution and rapid synchrotron X-ray powder diffraction measurement by combination of beam focusing optics, a flat shape sample and an area detector [1], was applied for diffraction experiments with anomalous scattering effect (anomalous diffraction). Generally, the combination of a flat shape sample and an area detector causes peak broadening by geometrical defocusing [2]. However, if incident X-rays are small enough in diffraction plane, diffraction peak width becomes narrow and high angular resolution will be achieved. We tried FFM using a large radius Debye-Scherrer camera of BL15XU at Spring-8 and verified that FFM practically gave high resolution and high quality powder diffraction data enough for atomic coordination refinement by Rietveld method. Angular resolution evaluated by Δd/d values calculated from NIST-CeO₂ powder diffraction pattern were equivalent to that of Debye-Scherrer mode of the diffractometer with the sample filled into 0.1 mmϕ capillary [1]. Fig. 1 shows the schematic view and the experimental setting of the diffractometer for FFM.

With anomalous diffraction using X-rays near absorption edge energy, we can distinguish neighboring atoms or different valence ions of an atom in crystal structure by difference of anomalous scattering factors. Thus the method has been widely applied to determination of site distribution or ordering structure of such atoms or ions.
An advantage of FFM for the anomalous powder diffraction is that FFM can avoid absorption problems in contrast to the capillary method. The geometry of FFM is a fixed-incident-angle asymmetric-diffraction. The flat shape powder sample was kept at a fixed angle throughout the measurement. The pass length of incident and diffracted X-rays through the sample determines the absorption amount of this geometry, which was investigated by James (1967) [3] and Toraya (1993) [4] as an asymmetric diffraction effect. The asymmetric diffraction effect can be described by a formula without approximations. Therefore the intensity data obtained by FFM does not include ambiguity of absorption. FFM is suitable for absorption sensitive experiments like anomalous diffraction.

FFM will improve the following point of anomalous diffraction experiments.
(1) The absorption correction without approximation gives diffraction intensity data without ambiguity.
(2) Rapid measurement with area detectors enables us to obtain many diffraction data sets with various energy X-rays in short time.
(3) High brilliance incident beam by focusing optics gives good signal-to-noise ratio diffraction data and makes it possible to detect small contribution of anomalous scattering effect.

Single crystal diffraction methods were preferred for anomalous diffraction because of correctness and good signal-to-noise ratio of diffraction intensity. However, intensity data collection from single crystals sometimes suffered from (1) absorption problem by sample shape, (2) twinning and/or domain problem and (3) low quality of single crystals caused by difficulty of synthesis. FFM is free from absorption problem as stated. The twinning and/or domain problem also can be ignored because FFM is a powder diffraction. Further, the synthesis of powder samples is sometimes easier than that of single crystals. We conducted synchrotron anomalous powder diffraction experiments to examine the possibility of FFM to apply for anomalous diffraction.

2. Experiments
The powder diffraction experiments were carried out at BL15XU at SPring-8. The synchrotron radiation from the planer mode of the undulator were monochromatized by a liquid-nitrogen-cooling Si(111) double-crystal monochromator. An X-ray total reflection double mirror system with Cr-coated flat mirrors was applied for reduction of higher harmonics. The 2nd mirror was bent to focus X-rays vertically to the rotation center of the diffractometer on flat shape samples. The distance between the 2nd mirror and the sample was 3.3 m. The focused beam size in vertical direction was determined as 0.032 mm by slit scanning. The diffraction peak width of FFM was calculated as 0.018 degrees at 2θ = 12 degrees by convolution of incident beam divergence (0.312 mrad) and diffracted X-ray width [2]. The beam divergence and diffracted beam width were evaluated by the geometry of beamline optics and FFM. The observed diffraction peak width was larger than expected from the geometry of FFM. The diffraction width of the powder sample was dominant for the diffraction peak width.

X-ray powder diffraction data were collected with the Debye-Scherrer camera of BL15XU. The camera is equipped with a cylindrical shaped imaging plate (IP) with the radius of 955 mm [5] as a detector. The use of the IP and the large camera radius enabled us to collect high angular resolution...
diffraction data in a short measurement time. The sample powder was spread on a flat sample holder with a diameter of 40mm and a depth of 0.5mm set at the center of the camera instead of the capillary sample holder. The fixed angle of incident X-rays was 7 degrees. The sample holder was rotated around an axis normal to the sample surface at a rate of 0.5 rot/sec to increase powder sample randomness during the measurement.

The read-out pixel size of the IP was 0.05 mm squares and the size corresponded to the 0.003 degrees in 2θ. An exposure on the IP covers 22 degrees in 2θ, therefore 5 exposures were carried out at 11, 30, 49, 55 and 64 degrees in order to obtain a whole powder diffraction pattern up to 70 degrees. The exposure time for each step was 10 seconds and total measurement time for a diffraction pattern was within a few minutes including mechanical movement. The change of incident X-ray energy with beamline optics was the bottleneck of the present experiments, however, we could obtain the data at 4 X-ray energies in a few hours. The anomalous diffraction experiment by FFM was not a beamtime-consuming experiment. The separately collected powder diffraction data recorded using an IP were connected and translated to 2θ-intensity format [5]. Correction for asymmetric diffraction [3,4] was carried out before further analysis.

Powder reagents of CoFe$_2$O$_4$ and Fe$_3$O$_4$ were prepared for powder diffraction experiments. Both compounds have inversed spinel structure, which can be described as B$^{IV}$(A$^{VI}$B$^{VI}$)O$_4$, where the overscripts IV and VI indicate the coordination number of atoms. In the present case, the A and B correspond to Cr$^{2+}$/Fe$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$ in CrFe$_2$O$_4$ and Fe$_3$O$_4$, respectively. Therefore, the octahedral sites take mixed valence state of Cr$^{2+}$/Fe$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$ in these compounds. We attempted to detect the diffraction intensity change reflecting the difference of anomalous scattering factors of those atoms and ions by the FFM.

The diffraction experiments were performed using lower energy X-rays than that of K absorption edge of the Fe metal. The point with the maximum differential of the absorption coefficient was determined as the Fe metal K edge in the observed X-ray absorption spectrum of a Fe metal thin film. The energy of the K edge was defined as 7.1112 keV, which was calculated by Sasaki (1986). The X-rays with energies 0, 3, 10, 200 eV lower than that of the K edge was used for the diffraction

![Fig.2 Change of powder diffraction intensity of CoFe$_2$O$_4$ and Fe$_3$O$_4$ obtained by the FFM against the change of incident X-ray energy. (a) 400 and (b) 222 for CoFe$_2$O$_4$ and (c) 400 and (d) 222 for Fe$_3$O$_4$. The intensities were normalized by that of 311 reflections.](image-url)
experiments. The use of lower energy X-rays than the K edge prevented increase of background noise caused by fluorescence X-rays.

3. Results and Discussions

Fig. 2 shows the change of the powder diffraction intensity of CoFe₂O₄ and Fe₃O₄ obtained by FFM against the change of incident X-ray energy. The intensities were normalized by the peak intensity of 311 reflection. (a) and (b) shows the 400 and 222 reflections of CoFe₂O₄ and (c) and (d) shows the same reflections of Fe₃O₄. The change of diffraction intensity as the change of incident X-ray energy were obviously observed. Both of CoFe₂O₄ and Fe₃O₄ have inverse spinel structure and cation sites take mixed valence state. Intensity of anomalous diffraction near absorption edge depends on the averaged anomalous scattering factors determined by cation distribution and incident X-ray energy. Therefore the cation distribution of spinel structure can be determined by detailed analysis of diffraction intensity change as the incident X-ray energy. Further, this method can be applied for determination of similar distribution or ordering of cations for other crystal structures.

The observed diffraction intensity change was compared with the calculation for CoFe₂O₄. The calculated atomic scattering and anomalous scattering factors of Co, Fe and O near Fe K edge by Sasaki [6] were adopted for the calculation. The atomic coordination data of CoFe₂O₄ including Co-Fe distribution between tetra- and octa- hedral site was taken from Yunus et al. [7]. A crystallographic information calculation program, Crystallographica (Oxford cryosystems), was used for powder diffraction intensity calculation. The calculated and observed intensities were normalized by intensity of 311 reflection. Fig. 3 shows the comparison of the observation and the calculation of intensity of 400 reflections. The observed and calculated diffraction intensity was consistent. The present results show that the powder diffraction by FFM can obviously and properly detect the difference of diffraction intensity by anomalous scattering effect neighboring atoms. FFM is expected to be a method for anomalous powder diffraction.

Fig 3. Comparison of calculated and observed powder diffraction peak intensity of 400 reflection of CoFe₂O₄ obtained by the FFM for X-rays around Fe-K edge energy. The line is a guide to eyes.

References
[1] Tanaka M et al 2009, 10th International Conference on Synchrotron Radiation Instrumentation, 597.
[2] He B B 2009 Two-Dimensional X-ray Diffraction (New Jersey: Wiley) pp 199-201
[3] James R W 1967 The Optical Principles of the Diffraction of X-rays (London: Bell) pp 44-52
[4] Toraya H, Huang T C and Wu Y 1993 J. Appl.Cryst. 26 774
[5] Tanaka M, Katsuya Y and Yamamoto A 2008 Rev. Sci. Instrum. 79, 075106
[6] Sasaki S 1989 KEK-Report 88-14
[7] Yunus S M et al 2008 Journal of Alloys Compd. 454 10