Application of Small-Angle X-ray Scattering Utilizing X-ray Anomalous Dispersion to Nano-Structure Analysis

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Small angle X-ray scattering utilizing with X-ray anomalous dispersion effect is performed for a system with periodically locating anomalous atoms. A peak indicating the periodic structure disappears around the absorption edge. Because one of the anomalous form factors, f', shows negative divergence at the absorption edge, the contrast for X-ray between the domain including the anomalous atom and the others also disappears. This result indicates that it could be possible to control the scattering power of a domain with an anomalous atom and observe the distribution of the anomalous atoms with this new scattering technique.

Key words : small angle X-ray scattering, X-ray anomalous dispersion effect

1 INTRODUCTION

In recent years, much interest has been focused on functional materials with nano-scale structure. Under this circumstance, it becomes more important to reveal the structures of these materials for newly development and improvement of their properties.

Small-angle X-ray scattering (SAXS) is one of powerful tools to investigate the structures in this scale. SAXS intensity, I(q) (q; a scattering vector), is expressed as follows¹).

$$I(\boldsymbol{q}) = \left| \int (\rho(\boldsymbol{r}) - \bar{\rho}) \exp(i\boldsymbol{q} \cdot \boldsymbol{r}) d^3 \boldsymbol{r} \right|^2 (1)$$

$$\rho(\mathbf{r}) = \sum_{i} f_{i}, \qquad (2)$$

where $\rho(\mathbf{r})$ and $\bar{\rho}$ are an electron density at position \mathbf{r} and its average, respectively, and f_i is an atomic form factor of the *i*-th atom and sum is taken over the atoms in the SAXS resolution range. Equation (1) means that a spatial fluctuation of electron density can be observed through the SAXS measurement. As an origin of the fluctuation, two candidates are supposed: one is a density fluctuation and the other is a heterogeneous distribution of the atoms and/or molecules. For examples, the former is a thermal fluctuation in a liquid consisting of a single component and the later is a phase separated structure by two/or more components.

Unfortunately, it is difficult to distinguish between two electron density fluctuations only with a standard SAXS method. Therefore, our purpose is to find out a method to be able to distinguish these two fluctuations. Here, we propose as one answer to utilize X-ray anomalous dispersion effect: the X-ray anomalous dispersion effect could derive a distribution of anomalous atoms from the fluctuation of the electron density distribution, which is observed with the standard SAXS method. Up



Fig. 1. Atomic form factor of Fe around the K absorption edge: f'(E) and f''(E) are the real and imaginary parts of the anomalous terms, respectively. f_0 is 26, independent of X-ray energy.

to now, the X-ray anomalous dispersion effect is usually utilized to solve a phase problem in a X-ray crystal structure analysis for a large molecule such as a protein: the method is called "MAD" (multi-wavelength Anomalous Diffraction)^{2,3)}. On the other hand, we have made an attempt to utilize the X-ray anomalous dispersion effect in SAXS method by sweeping the incident X-ray energy around the absorption edge of the anomalous atom⁴⁾.

In this paper, in order to examine a SAXS method utilizing X-ray anomalous dispersion effect, a simple one-dimensional system where the anomalous atoms periodically locate is observed by sweeping an X-ray energy around the absorption edge.

2 X-ray anomalous dispersion effect

In a standard SAXS experiment, form factors of all atoms in a system are treated as constants. On the other hand, the form factor of a selected atom should be variable in our method because an incident X-ray energy should be varied around the absorption edge of the selected atom.

By taking an X-ray anomalous dispersion effect into account, the atomic form factor f(E) is written as follows.

$$f(E) = f_0 + f'(E) + i f''(E), \qquad (3)$$

where f_0 is proportional to the total number of electrons in the atom and is independent on the energy of the incident X-ray. In contrast, f'(E) and f''(E), "anomalous dispersion terms", depend on the incident energy, in particular near around the absorption edge.



Fig. 2. Chemical structure of dodecylferrocenecarboxylic potassium (DFCP).

In Fig. 1, the form factors of an Fe atom are shown as a function of an incident Xray energy around the Fe-K absorption edge at 7.1109 keV⁵). The notable features are steeply negative divergence of f'(E) and step function-like behaviour of f''(E) at the absorption edge. The former feature means that we could selectively change $\rho(\mathbf{r})$ of the domain including Fe atoms. In other words, we can observe the distribution of only the domain including Fe atoms in the system by the SAXS experiment sweeping the energy of incident Xray around the Fe absorption edge.

3 EXPERIMENT

3.1 Sample

Dodecyl-ferrocenecarboxylic potassium (DFCP), of which chemical structure is shown in Fig. 2, was synthesized for the sample with an anomalous atom, Fe. DFCP makes microphase separation between domains of alkyl chains and carboxylic potassium, and forms one-dimensional structure, lamella⁶. It means that Fe atoms periodically locate in the system.

3.2 Small-angle X-ray scattering with energy sweep

A synchrotron light (SL) is a suitable Xray source of our SAXS method with energy sweep because one of the features of SL is Xray source with wide wavelength range. SAXS measurements sweeping the energy around the Fe-K absorption edge were performed at BL10C of Photon Factory, synchrotron light facility in High Energy Accelerator Research Organization (KEK), Tsukuba Japan. The SAXS intensities were measured in the sweep range of X-ray energy between 7.07-7.15 keV with an energy step of 20 eV. The energy of the incident X-ray was tuned with double monochromatores of Si with a resolution $\Delta E/E \simeq 10^{-4}$. The scattered X-ray was detected with a one-dimensional detector and the intensity was accumulated for 600 sec at



Fig. 3. SAXS profile of DFCP. Energy of an incident X-ray is set to be 8.33 keV (1.488 Å), which is an absorption edge of Ni.

each energy scanning step: the corrections were made for absorption by the specimen and for the decay of the orbit current of the synchrotron.

4 RESULTS AND DISCUSSION

4.1 Lamellar structure of DFCP

Before starting an energy sweep SAXS experiment, we examined the structure of DFCP with a standard SAXS experiment. Figure 3 shows a SAXS profile of DFCP observed with 8.33 keV X-ray (Ni-K absorption edge) which was far from Fe-K absorption edge (7.11 keV). Therefore, we can ignore an anomalous dispersion effect of an Fe atom.

An intensive peak was observed at 1.97×10^{-1} Å⁻¹, indicating that there exists a periodic structure with an interval of 31.9 Å, $d = 2\pi/q$. This value shows a good agreement with the published datum⁶). As mentioned before, the lamellar structure could be formed by the microphase separation between alkyl chains and carboxylic acid. Therefore, Fe atoms in ferrocene molecules also locate periodically with the same interval of the lamella.

4.2 Transmission

To examine the performance of the SAXS spectrometer for the energy sweep experiment, firstly, we observed the transmission of DFCP around the Fe-K absorption edge. Figure 4 shows the energy dependence of transmission of DFCP in the energy range between 7.07 and 7.15 keV: the Fe-K absorption edge is 7.1109 keV. The transmission drops at the Fe-K absorption edge with increasing of the inci-



Fig. 4. Energy dependences of observed transmission of DFCP and calculated linear absorption coefficient of Fe atom. Solid line indicates the calculated linear absorption coefficient of Fe.⁵) Closed circles denote the observed transmission of DFCP and a broken line is eye guide.

dent X-ray energy. It is reasonable because an absorption power of Fe steeply increases at the Fe-K absorption edge as shown in Fig. 4 (see a solid line)⁵⁾. Accordingly, the spectrometer can sweep the energy ranges across the Fe-K absorption edge with the fine energy resolution and the sample has an enough amount of Fe atoms for observing the anomalous dispersion effect.

4.3 Anomalous dispersion effect

Figure 5 shows energy dependence of the peak intensity, indicating the periodical distance of the lamella structure. Approaching to the Fe-K absorption edge (7.1109 keV) from the lower energy (7.07 \rightarrow 7.11 keV), the peak intensity slightly became decrease and then the peak disappeared at the energy (7.13 keV) just higher than the absorption edge. As the further increase of the energy, the peak reappeared at the same q position of 7.15 keV.

As shown in Fig. 3, the sample showed a sharp peak in the SAXS profile observed at Ni-K absorption edge (8.33 keV), where we can ignore the anomalous dispersion effect of Fe. Therefore, the peak comes from the difference of the electron density between the domain of ferrocenecarboxylic potassium and that of alkyl chains: An Fe atom in a ferrocene mainly accounts for the higher electron density in the domain of ferrocenecarboxylic potassium. In the narrow energy window $\Delta E \leq 20$ eV around the Fe absorption edge, an only atomic form factor of an Fe atom becomes small because f'(E) makes negative



Fig. 5. Energy dependence of of peak profiles $(q \sim 0.02 \text{ Å}^{-1})$ of DFCP around the Fe-K absorption edge (7.1109 keV). The profiles were normalized with the incident X-ray intensity and corrected with the transmissions.

divergence there (see Fig. 1). Therefore, approaching to the absorption edge, the difference of scattering power between the domain of ferrocenecarboxylic potassium and that of alkyl chains became small. At the absorption edge, the difference was eliminated and the peak disappeared as shown in Fig. 5.

The results mentioned above mean that the peak accounting for the structure with the anomalous atoms drastically changes in its intensity around the absorption edge. In other words, by observing a scattering profile with energy sweep around the absorption edge, we can extract the distribution of the only anomalous atoms from the scattering data. In addition, just close to the absorption edge, we can delete the anomalous atoms in the scattering and could observe the fine structure hidden by the scattering from the relatively heavy anomalous atoms: the shoulders were observed in the peak profiles at the several Xray energy (7.09, 7.11, and 7.15 keV). This could be similar to the contrast variation in neutron scattering¹). However, our experimental resolution for energy ($\Delta E = 20 \text{ eV}$) is not enough to make sure of this possibility. More detailed experiments are now in progress.

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