Anomalous scattered X-rays observed in the soft X-ray region

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ABSTRACT

Anomalously intense scattered X-rays are observed in the soft X-ray region, when a special experimental set-up was adopted; grazing X-ray incidence and nearly normal X-ray emission for a microcrystalline sample. Although the origin of the phenomenon has not been clarified yet, it was confirmed that it is not an experimental artifact, but is intrinsic and something to do with mesoscopic structures of microcrystalline samples.

1. Introduction

When X-rays irradiate a solid sample, various phenomena take place, such as scattering, diffraction if the sample has long range orderings, absorption which causes electron emission, fluorescent X-ray emission, and ion desorption, etc. Analyses of the angular and energy distributions of these X-rays and/or electrons provide useful information of atomic and electronic structures, as are known as well-established methods[1]. We have been working on XAFS in the soft X-ray region with electron yield and fluorescence yield methods. The latter method is especially useful for a sample with low concentration, but it sometimes suffer from high backgrounds due to scattering X-rays. Thus, it is important to suppress scattering X-rays to obtain reliable XAFS spectra. In the hard X-ray region ($h\nu>4$ keV), the behavior of scattered X-rays have been extensively studied[1]. In contrast, a few studies have been done in the soft X-ray region ($h\nu< 1$ keV) [2,3], but no in the higher soft X-ray region ($h\nu =1\sim4$ keV), as far as the authors know. Thus, we have investigated the angular and energy distributions of scattered X-rays, and the effects of the energy and angle of incident X-rays. In the study, we happened to find anomalous X-rays emitted from a powdered sample only at a special experimental arrangement.

2. Experimental

All the experiments have been performed in the SR center, Ritsumeikan University, at the soft X-ray double crystal monochromator beamline (BL-10)[4,5]. The synchrotron radiation beam is focused with a toroidal mirror onto a sample position. In between the mirror and the sample, a Golovchenko-type double crystal monochromator is located to provide monochromatic beam, ranging from 1 ～ 4 keV, by changing a crystal pair; Beryl(1010), Quartz (1010), InSb(111) and Ge(111). The experimental set-up is shown in Fig. 1, where the direction of an X-ray detector is perpendicular to that of the incident beam. SDD (silicon drift detector) with an effective detecting area of 5 mm^2 (KETEK Ltd.) was used as the X-ray detector, apart from the sample center by 30 mm. The incident angle of the monochromatic beam was changed and the scattered X-rays were detected with the SDD. All the samples are powdered, dispersed on a carbon tape and mounted on a sample holder, shown in Fig. 1.

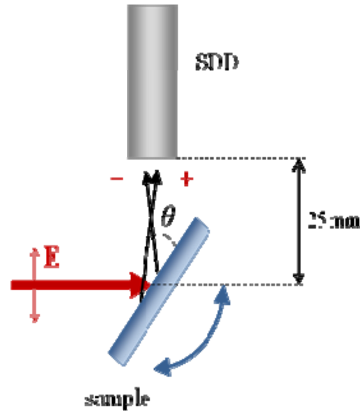

Fig. 1. Experimental lay out for the soft X-ray scattering

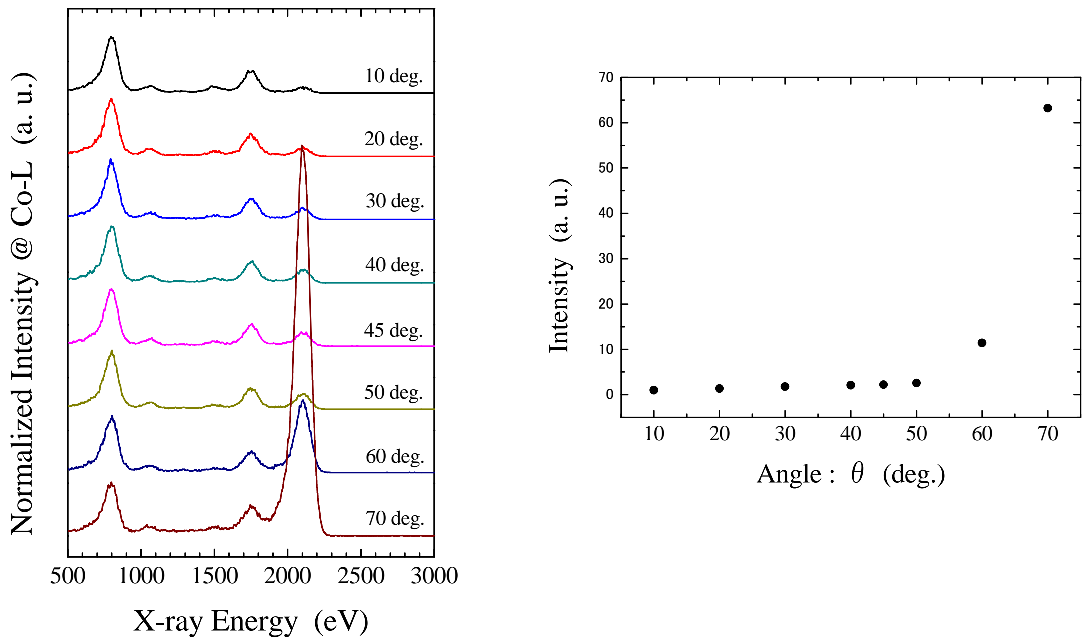

Fig. 2 (a) Fluorescent X-ray energy distribution from microcrystalline powder of $LiCoO_2$.

(b) Integrated intensity plots of the elastic peak as a function of the incident angle.

3. Results and Discussion

Figure 2(a) shows the fluorescent X-ray profiles from microcrystalline powder of $LiCoO_2$ at several incident angles. Three peaks appear in the spectra, at 750, 1800, and 2100 eV. The first and second features are from Co L and Si K (impurity), respectively and the third one is due to the elastic scattering. In Fig. 2(b), the intensity of the elastic scattering peak from $LiCoO_2$ is plotted as a function of the incident angle. For comparison, the scattering peak intensity from a Si wafer is also plotted, where the

incident photon energy was 1800 eV. As the sample area irradiated by X-rays increase with the incident angle, the intensity of the elastic peak should increase, roughly in proportional to 1/cosθ, as in the case of the Si wafer. In contrast, the scattering peak from $LiCoO_2$ gains intensity dramatically at the grazing incidence.

We also measured other samples, such as microcrystalline samples of CoO, Li_2MnO_2 and MnO_2 and found a similar tendency, although the extent of increase differs from each other, depending on the sample.

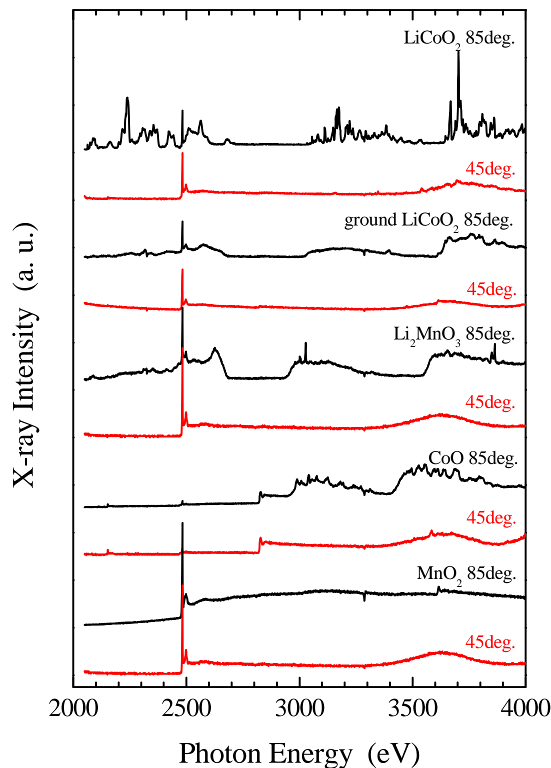

Fig. 3 Fluorescent X-ray yield spectra from several metal oxides for two incident angles, 45° and 85°. The third spectrum from the top is one taken after grinding the powder $LiCoO_2$ (the top spectrum) for 1 hour at the incident angle of 85°.

To confirm that this phenomenon is not an artifact, we studied the fluorescent X-ray yield as a function of the incident photon energy for each sample, where all the photons with the energy higher than 2000 eV were collected by using a discriminator. Figure 3 shows two spectra at the incident angles of 85° and 45° for each sample ($LiCoO_2$, Li_2MnO_2, CoO and MnO_2). The spectra at the incident angle of 45° and emitted angle of 45° show K edge absorption peaks from P, S and Cl impurities and a broad band at around 3600 eV, which can be due to fundamental powder diffraction peaks. For

example, $LiCoO_2$ has a rhombohedral R3m structure, whose unit cell in the hexagonal setting shows a=b=2.8 Å and c=14.0 Å[6]. In the powder X-ray diffraction pattern (λ= 0.5 °), the second lowest peak appears at 12.3° in 2θ, which is assigned to (006). In the present experimental setup, θ is kept to 45° and the peak should appear at 3.3 Å (3758 eV) in the X-ray energy scale, which corresponds to the broad band peaked at 3700 eV.

In the spectra at the incident angle of 85° and emitted angle of 5°, additional broad peaks are superimposed on the spectra at 45°with sharp structures. In particular, the spectrum from $LiCoO_2$ shows many sharp structures, which are in contrast with broad features associated with powder diffraction.

These sharp structures are reproducible and highly dependent on the sample position. Figure 4 shows the spectral profiles as a function of the sample position. The monochromatic X-ray beam has a size of 4 mm^H x 1 mm^V at the sample position, and the sample was lifted up in the step of 0.05 mm. S K-XAFS spectra do not change at all by changing the sample position, but the scattered X-rays drastically change their intensity, indicating that they are sharp X-ray spots.

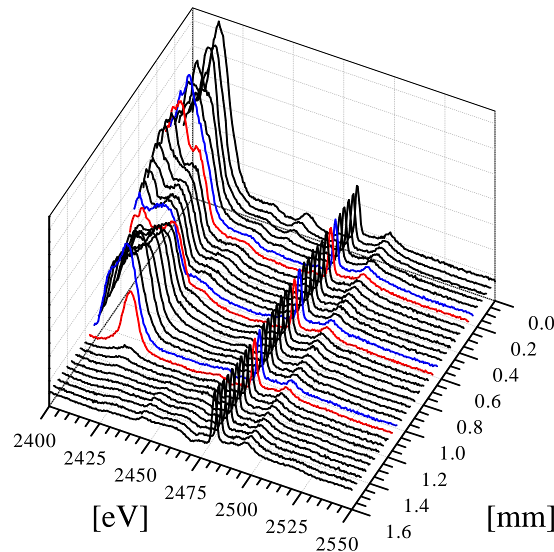

Fig. 4 A part of scattered X-ray profiles as a function of sample height. Sharp peak and following fine structure starting at 2478 eV are S K-XAFS of impurity sulfur. The profile at around 2400 eV is due to scattered X-rays.

To investigate the origin of these sharp structures, we examined the effect of grinding microcrystalline samples. Figure 5 shows SEM images of the $LiCoO_2$ sample before and after grinding in a mortar with pestle for 1 hour. Average particle size becomes clearly smaller by grinding. Figure 6 is the spectra before and after grinding. By making

particle size smaller, sharp structures disappear and rather broad structures are seen.

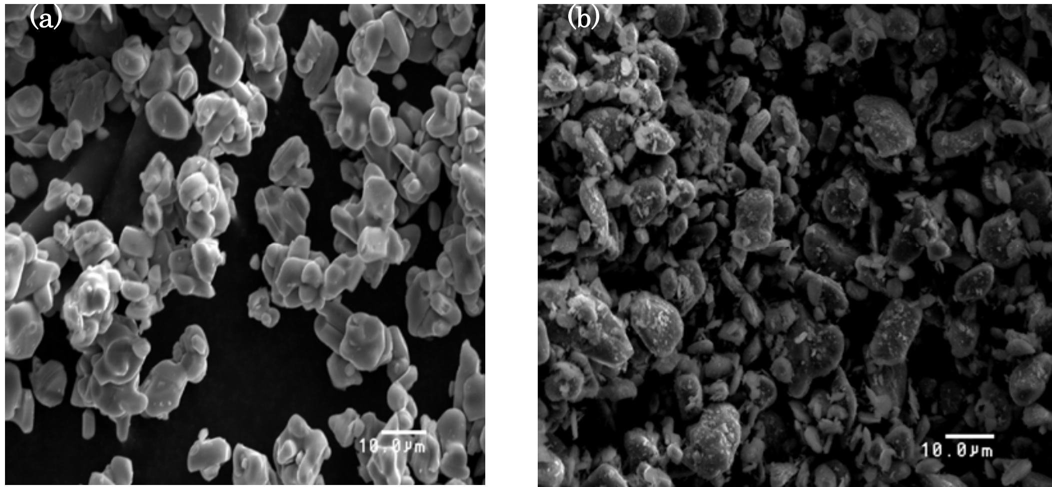

Fig. 5 SEM images of powdered $LiCoO_2$ before grinding (a) and after grinding (b)

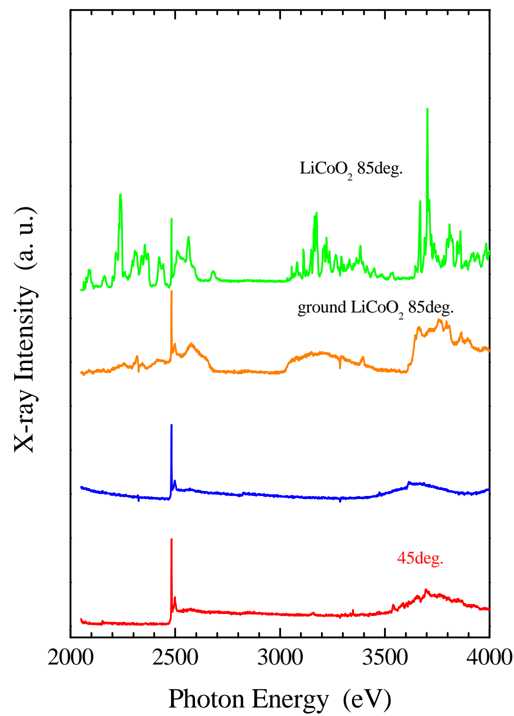

Fig. 6 Energy distribution profiles of $LiCoO_2$ before and after grinding. Top two profiles are those with grazing incidence before and after grinding. Bottom two profiles are those with an incident angle of 45° before and after grinding.

This result suggests that these sharp structures are closely associated with microcrystalline structures.

As described above, we found several abnormal results.

(1) The scattering X-rays gain their intensity tremendously at the grazing incidence and nearly normal emission setup.
(2) Sharp structures appear in the X-ray yield spectra, whose intensity changes sensitively with the sample position.
(3) The sharp structures are associated with mesoscopic structure of a sample.

Although the origin of these anomalous scattered X-rays is not clarified yet, it is not an experimental artifact and would be a sensitive probe of a mesoscopic structure.

Acknowledgement

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