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Spectro-Diffractometry for Chemical-State Analysis Based on In-Advance Simulations

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We performed an in-advance simulation and experiments involving resonant X-ray powder diffraction with the incident X-ray energy being near to the absorption edge of a particular element in order to distinguish two chemical states of that element based on the principle of spectro-diffractometry. According to the simulation, we found reflections that are relatively sensitive to the exchange of the two anomalous scattering factors (f') of the specified element at two crystallographic sites. The simulation and experiment results demonstrated that it is possible to obtain f' curves for the two chemical states by measuring only a few peaks that are sensitive to f' without greatly increasing the refinement errors, and that the way of selecting the peaks greatly influence the results. In other words, in-advance simulations are very important in this method. This method may make it possible to obtain nearly the same result in one-tenth machine time, and, moreover, to obtain site-selective XANES for powder samples using limited machine time.

A nondestructive chemical-state analysis is very important in materials, environmental, biological, clinical, and toxicological sciences. With the increasing availability of high-resolution powder diffractometers at many synchrotron-radiation facilities throughout the world, there is growing interest in the exploitation of anomalous-dispersion techniques for chemical-state studies of polycrystalline materials.[1,2] The use of powder-diffraction methods offers an attractive alternative in cases where single crystals are not available, and is less prone to beam instabilities and instrumental-alignment problems.

In conjunction with the Rietveld method[3] for structure refinement, there is a possibility to distinguish between different oxidation states of a particular element in a compound. Though this technique requires careful measurements at wavelengths very close to an absorption edge, a direct assignment of each oxidation state to a specific site in the structure can be made, which is seldom possible with any spectroscopic technique. This approach may be called spectro-diffractometry. In fact, the use of powder diffraction for such experiments has been demonstrated for Eu_3O_4,[4] $YBa_2Cu_3O_{6+x}$,[5] Ga_2Cl_4,[6] α-Fe_2PO_5,[7] and $YBa_2Cu_3O_y$.[8] However, when using the same machine time, how to obtain enough f' values without greatly increasing the refinement errors is still a great problem to be considered. In the present work, an in-advance simulation method was introduced to cope with this problem. This method make it possible that measurements of only a few selected reflections will be sufficient to obtain the f' curves for the two different states if the crystal structure parameters are known using the conventional method.

The Principle of Analysis

X-Ray diffraction results from the coherent scattering of X-rays by an ordered array of atoms. The atomic scattering factor (f) for X-rays contains a normal term (f_n) and an anomalous contribution (f_a), usually written as $f'+if''$; f' and f'' denote the real and imaginary parts of the anomalous scattering factor, respectively,

$$f(E)=f_n+f'+if''. \tag{1}$$

The normal scattering depends upon the electron distribution, and is independent of the X-ray wavelength, whereas the anomalous dispersion results from electronic transitions from core levels to unoccupied states, and is thus highly wavelength dependent. Generally, the determination of anomalous scattering coefficients from absorption or interferometric data uses bulk measurements, and thus gives values that are averaged over all the sites within a material. However, crystal-structure refinements offer the possibility of obtaining f' and f'' for each crystallographically distinct site occupied by the resonant element. Therefore, the anomalous scattering factors obtained from crystal-structure refinements are capable of providing information similar to that provided by X-ray absorption measurements through the optical theorem (Eq. 2)[9] and Kramers–Kronig dispersion relationships (Eqs. 3 and 4), but with the additional advantage that it is crystallographically site-selective.

$$f''(E) = \left(\frac{mc}{2he^2N}\right)\cdot E\cdot\mu(E), \tag{2}$$

$$f'(E) = \left(\frac{2}{\pi}\right)\int_0^\infty \frac{E^*\cdot f''(E^*)}{E^2 - E^{*2}}\cdot \mathrm{d}E^*, \tag{3}$$

$$f''(E) = \left(\frac{2E}{\pi}\right)\int_0^\infty \frac{f'(E^*)}{E^2 - E^{*2}}\cdot \mathrm{d}E^*, \tag{4}$$

where E is the energy, m is the electron mass, c is the velocity of light, h is Planck's constant e is the electron charge, N is the number density of atoms, and $\mu(E)$ is the linear X-ray absorption coefficient.

The diffraction intensities are dependent on $f = f_n + f' + \mathrm{i}f''$. The anomalous scattering factors, f' and f'', typically shift to higher energies by a few eV per oxidation-state unit, as shown in Fig. 1. Thus, in the resonant region, f' varies significantly, depending on the oxidation states. Therefore, a crystal-structure refinement makes it possible to obtain f' for each crystallographic site occupied by the resonant element. By careful measurements of the X-ray powder diffraction patterns near to the X-ray absorption edge of the specified element, the dispersion curves (f' curves) of that element at two different sites can be obtained through a Rietveld analysis. According to the relative shift of the two dispersion curves for the specified element at different sites, the distribution of the oxidation states for that element in compounds can be determined.

However, many powder diffraction patterns at energy points near to the absorption edge of the specified element must be collected to determine the f' curves for the two sites at which atoms with different oxidation states are located, respectively. The more precise are the f' curves, the greater must be the number of patterns. Consequently, it may require much machine time if the whole pattern is collected at many energy points. In order to collect the powder-diffraction data more effectively, in-advance computer simulations have been attempted to check which peaks in the spectra are more sensitive to the exchange of the anomalous scattering factor (f') of a particular element in different states. Based on the results of the simulations, we can choose some peaks to measure. In this way, more patterns near to the absorption edge could be collected with limited machine time and the precision of this kind of measurement may be improved.

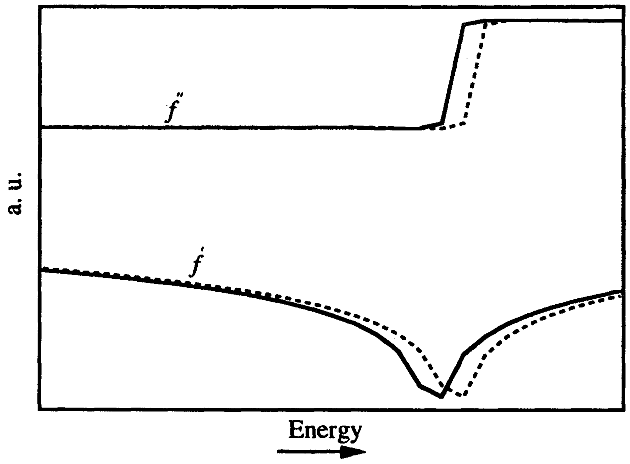

Fig. 1. Schematic illustration of the shift in the curve for f' and f'' as a function of X-ray energy from a lower (solid line) to a higher (dashed line) oxidation state.

Simulation

By comparing the calculated powder diffraction pattern of one structural configuration with another in which the specified element is replaced with the same element in different chemical state, it is easy to estimate which peaks on the diffraction pattern are more sensitive to the chemical states of the specified element. The difference between those two patterns is due to the rapid change of f' and the chemical shifts near to the absorption edge, as shown in Fig. 1.

The simulations for the X-ray powder diffraction pattern can be done using the RIETAN-97β software[10] if the crystal structural parameters are given (the structural information about the compound can be obtained by a conventional method). Based on the results of the calculation, it is possible to determine which peaks should be measured and which peaks could be skipped in experiments without any great statistical influence on the f' curves.

A Co_3O_4 powder specimen that crystallizes in the magnetite structure was used as an example. Co atoms exist at two distinct crystallographic sites, Co1 and Co2, in the magnetite structure. By assuming that the K edge of Co1 is 5 eV lower than the K edge of Co2, the incident X-ray energy was set at 7.702 keV to ensure that the X-ray energy is below both absorption edges of Co1 and Co2, since the absorption edge of Co1 is 7.709 keV. Choosing the X-ray energy in this way is just for convenience. It must be pointed out that in a simulation, how to choose the absorption edge is not important, because only the incident X-ray energy relative to the absorption edge has great influence on the simulation results. The real absorption edge for the specified element will be determined by experiments. For the values of anomalous scattering factors, f' and f'', a table calculated by Sasaki[11] was used (the values are listed in Table 1), which is based on the Cromer and Liberian theory.[12]

The simulated powder diffraction patterns are shown in Fig. 2 in which the solid line presents the pattern simulated according to the structure parameters obtained by Roth[13] and the anomalous scattering factors listed in Table 1, while the dashed line presents the pattern calculated after exchanging the anomalous scattering factor f' and f'' of Co1 and Co2. The difference between the two patterns is shown in the top

Table 1. Anomalous Scattering Factor f' and f'' for Co1 and Co2 for 7.702 keV X-Rays

	f'	f''
Co1	−8.368	0.473
Co2	−6.871	0.474
O	0.049	0.035

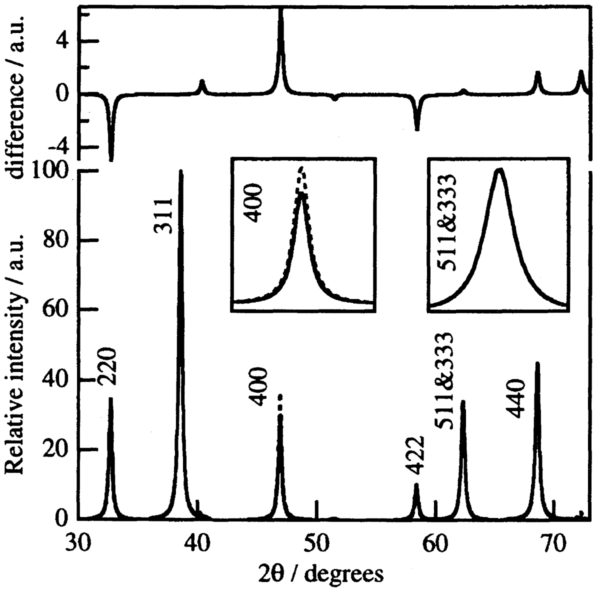

Fig. 2. Powder diffraction patterns simulated by software RIETAN-97β. Dashed line: the edge of Co1 is 5 eV lower than Co2; Solid line: the edge of Co1 is 5 eV higher than Co2. Upper is their difference and the insets are the enlarged 400 and 511 and 333 peaks.

of Fig. 2. The insets show enlarged 400 and 533&313 peaks. Based on the simulation result, it could be clearly seen which peak is sensitive to an exchange of the anomalous scattering factor (f') for the two Co sites. Here, the two patterns were normalized with respect to the strongest peak, 311.

Experimental

A conventional experiment was carried out to determine the crystal-structural parameters such as the lattice constant (a), the atomic position parameters (x, y, z) and the temperature factors (B). The X-ray pattern was obtained from Co_3O_4 powder specimens and Cu$K\alpha$ radiation using a M03XHF22 powder diffractometer manufactured by Mac Science Company.

Synchrotron-radiation powder diffraction patterns were obtained using the powder diffractometer for synchrotron radiation with a multiple-detector system at BL-4B2 of the Photon Factory in KEK. The sample was mounted on a flat plate holder and rotated so as to decrease the preferred orientation effect. The energy of the incident X-ray was chosen by a Si(111) monolithic monochromator, and its resolution was about 1 eV. According to the simulations mentioned above, 6 peaks were chosen to measure. The intense peaks were preferred when considering the statistical error. Table 2 lists the angles of these peaks that were calculated using RIETAN-97β for 6 energy points near to the absorption edge of cobalt. According to the FWHM (full width at half maximum) of the peaks, the 2θ angle range was 2 degrees around the peak position for 111, 220, 311, and 400 peaks, 2.2 degrees for 422 peaks, and 2.4 degrees for 511, 333 and 440 peaks. The experimental profiles for these peaks are shown in Fig. 3.

Results and Discussion

The Rietveld refinement profile for the conventional experiment is shown in Fig. 4. The refined structure parameters are listed in Table 3.

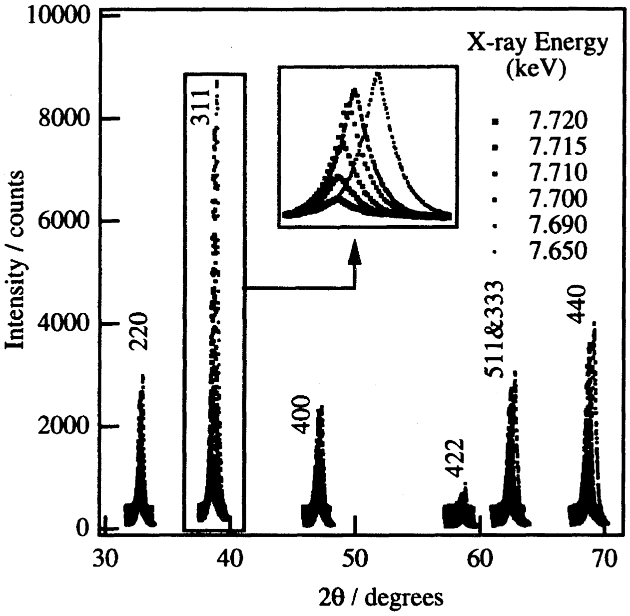

Fig. 3. Collected powder diffraction peaks for Co_3O_4 at 6 energy points near the absorption edge of Co.

Table 2. The Index and Angle of 6 Selected Peaks at 6 Energy Points

Energy (keV)	7.65	7.69	7.70	7.71	7.715	7.720
220	32.95	32.77	32.73	32.69	32.67	32.64
311	38.85	38.64	38.59	38.53	38.51	38.48
400	47.29	47.03	46.97	46.90	46.87	46.84
422	58.84	58.51	58.42	58.34	58.30	58.26
511, 333	62.80	62.44	62.35	62.26	62.21	62.17
440	69.11	68.70	68.60	68.50	68.45	68.40

Table 3. The Structure Parameters of Co_3O_4 Compounds Refined by Rietveld Analysis for Powder Diffraction Pattern Taken from the Conventional Diffractometer Radiation: Cu$K\alpha$

Co_3O_4 Space group: $F3dm$ (227), a=8.0837 Å					
	x	y	z	B	g
O	0.3881	0.3881	0.3881	0.1	1
Co1	0.0	0.0	0.0	0.4	1
Co2	0.625	0.625	0.625	0.6	1

To determine the anomalous scattering factors near to the absorption edge, a Rietveld analysis was used to refine the real part of the anomalous scattering factor (f') of Co1 and Co2. For the refinement of f', the source code of RIETAN-97β was modified.[14] In the analysis, we assumed that the imaginary part of the anomalous scattering factor (f''), is a simple step function, the values of which are determined only by the incident X-ray energy being below or above the absorption edge. The f'' values were obtained from a table calculated by Sasaki.[11] The measurement of the Co absorption edge for Co_3O_4 powder, as shown in Fig. 5, was used to determine the incident energy was below or above the edge.

f' and their estimated standard deviations determined from

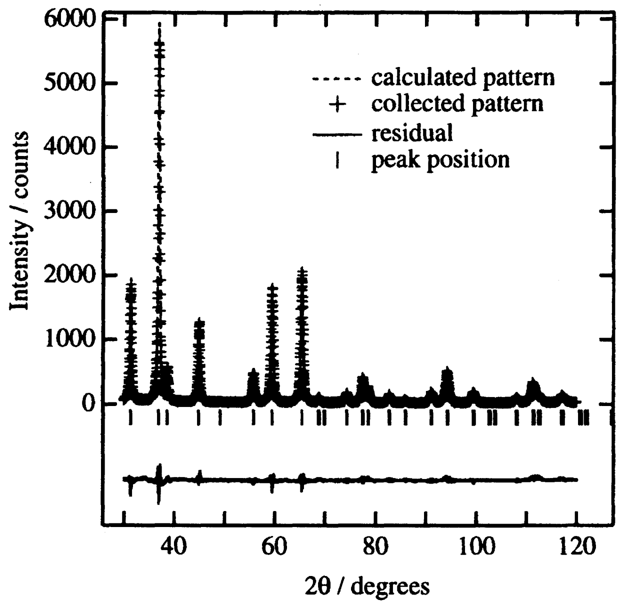

Fig. 4. Conventional X-ray powder diffraction pattern of Co_3O_4 and Rietveld fitting result.

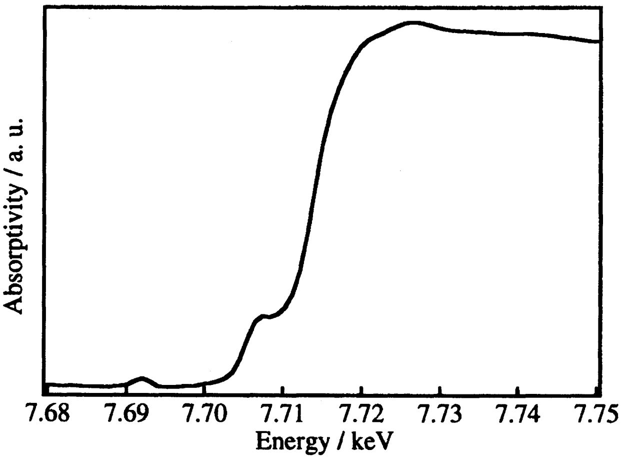

Fig. 5. Absorption spectra of Co_3O_4 powder near the absorption edge of Co. This figure was not normalized by the intensity of the incident X-ray. That does not affect the determination of the absorption edge.

Table 4. Values of f' Refined with 6 peaks by Rietveld Analysis

Figures in parentheses are estimated standard deviations in the last significant digits throughout this paper.

Energy (keV)	7.65	7.69	7.70	7.71	7.715	7.720
Col	−5.27 (0.08)	−6.37 (0.07)	−6.89 (0.11)	−7.91 (0.09)	−9.32 (0.11)	−8.7 (0.2)
Co2	−5.24 (0.12)	−6.23 (0.11)	−6.69 (0.16)	−7.72 (0.15)	−8.74 (0.18)	−9.7 (0.3)

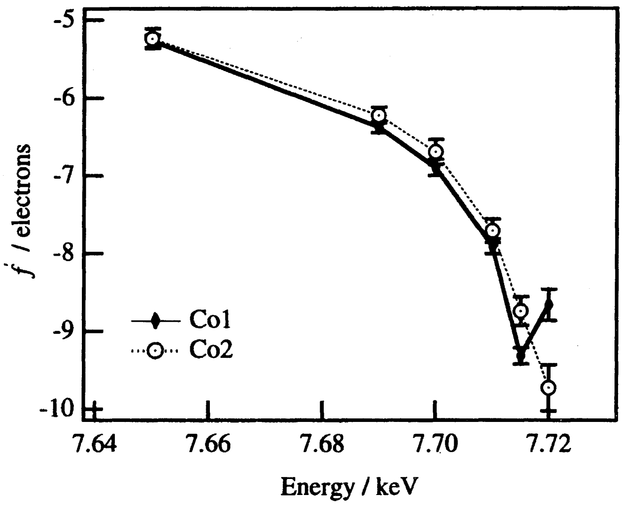

Fig. 6. f' refined with all 6 peaks in the powder diffraction patterns of Co_3O_4.

Table 5. Values of f' Refined with 3 Peaks (220, 311, 400) by Rietveld Analysis

Energy (keV)	7.65	7.69	7.70	7.71	7.715	7.720
Col	−5.5 (0.09)	−6.74 (0.13)	−7.32 (0.11)	−8.27 (0.10)	−9.72 (0.11)	−9.0 (0.2)
Co2	−5.52 (0.13)	−6.59 (0.11)	−7.2 (0.2)	−8.10 (0.14)	−9.2 (0.2)	−10.0 (0.3)

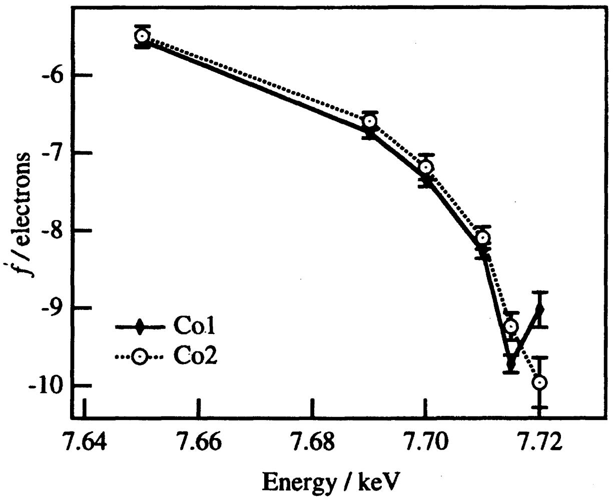

Fig. 7. f' refined with the appropriate set of 3 peaks (200, 311, 400) in the powder diffraction patterns of Co_3O_4.

all of 6 peaks (220, 311, 400, 422, 511(333), 440) are listed in Table 4 and shown in Fig. 6, while those determined from 3 peaks (220, 311, 400) are listed in Table 5 and shown in Fig. 7. Those determined from other two different sets of 3 peaks (311, 511 and 333, 400) and (311, 400, 511 and 333) are listed in Tables 6 and 7 and shown in Figs. 8 and 9, respectively.

From the results obtained, respectively, from all of 6 peaks and the first 3 peaks (220, 311, 400), it could be clearly seen that there is no great change between the two results. Especially, the differences between the two f' values and the standard deviations almost remain unchanged at each energy point. Therefore, it can be said that only a few peaks in the powder diffraction pattern may be sufficient to obtain

Table 6. Values of f' Refined with 3 Peaks (400, 511 and 333, 440) by Rietveld Analysis

Energy (keV)	7.65	7.69	7.70	7.71	7.715	7.720
Co1	−4.4	−5.0	−5.8	−6.7	−9.3	−9.0
	(0.4)	(0.3)	(0.5)	(0.5)	(0.7)	(1.1)
Co2	−4.3	−4.6	−5.5	−5.5	−3.2	−7.3
	(0.6)	(0.6)	(0.8)	(0.9)	(1.3)	(1.9)

Table 7. Values of f' Refined with 3 Peaks (311, 400, 511 and 333) by Rietveld analysis

Energy (keV)	7.65	7.69	7.70	7.71	7.715	7.720
Co1	−5.68	−6.51	−7.1	−7.93	−9.0	−8.6
	(0.16)	(0.14)	(0.2)	(0.16)	(0.2)	(0.5)
Co2	−5.7	−5.8	−6.6	−6.8	−5.0	−8.5
	(0.5)	(0.5)	(0.7)	(0.7)	(1.1)	(2.0)

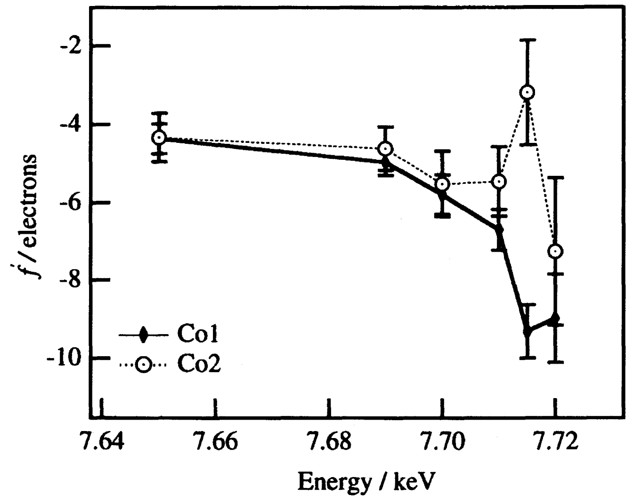

Fig. 8. f' refined with the second set of 3 peaks (311, 511 and 333, 440) in the powder diffraction patterns of Co_3O_4.

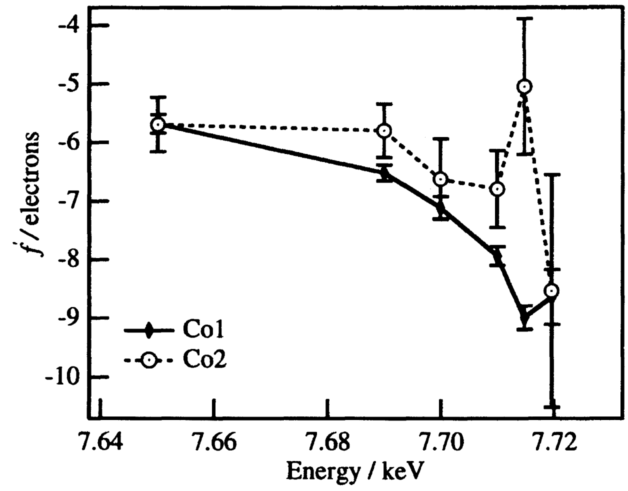

Fig. 9. f' refined with the third set of 3 peaks (311, 400, 511 and 333) in the powder diffraction patterns of Co_3O_4.

the anomalous scattering factor (f'). Here, in addition to the most intensive peak (311 in this work), we should select two more peaks which show the largest and the second largest differences in the simulated pattern intensity. However, f' determined from the second 3 peaks set (311, 511 and 333, 440) came along with large standard deviations. This means that how to select 3 appropriate peaks among 6 peaks is quite important. From the simulation results shown in Fig. 2, it has been found that the first set of 3 peaks is sensitive to changes in the anomalous scattering factor, while the second set of 3 peaks is not. Although it has been attempted to determine the f' values using the third set of 3 peaks, the most intensive peaks (311), peak 400 with the largest difference and peaks 511 and 333 with almost no difference, f' values that are better than those determined from second set of 3 peaks, but not so good as those determined from the first set of 3 peaks were obtained. From the simulation result shown in Fig. 2, it can be found that the first set of 3 peaks is more sensitive to the exchange of the anomalous scattering factor than the later two sets, while the third set is more sensitive than the second set. Thus, in order to obtain the correct f' values, it is important to select the appropriate set of three peaks.

The greater standard deviations for the f' data above the absorption edge may be attributed to low statistical counts caused by the intense fluorescence effect.

The refinement of the f' values from any two peaks resulted in unbelievable large standard deviations (10—10^6 electrons). Those large standard deviations may result because the number of the unknown values, two f' and one scale factor, is larger than the number of peaks. Therefore, choosing more than 3 peaks was strongly recommended.

Conclusions

In-advance simulations and experiments were performed for resonant powder diffraction with the incident X-ray energy being near to the absorption edge of a specified element.

(1) According to the simulation, there are peaks that are greatly influenced and peaks that are slightly influenced by an exchange of the oxidation state of a specified element.

(2) The experimental results reveal that it is possible to determine f' by measuring only a few peaks that are sensitive to the anomalous scattering factor without greatly increasing the errors.

(3) From the experimental results, it is clearly seen that the way to select peaks is very important, and, therefore, the importance of an in-advance simulation was proved.

(4) This method may make it possible to obtain nearly the same result in one-tenth the machine time, and, moreover, to obtain site-selective XANES (X-ray absorption near-edge structure) for powder samples using limited machine time.

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