In-Advance Simulation and Chemical State Analysis by Spectro-Diffractometry

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In-advance simulation and experiment were performed for resonant powder diffraction with the incident X-ray energy near the absorption edge of a particular element to distinguish two chemical states of that element. The simulation and experimental results demonstrated that it is possible to obtain the f' curves for the two chemical states by measuring only a few peaks that are sensitive to f' without increasing refinement errors greatly.

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 suitable crystals are not available, and is less prone to beam instabilities and instrumental alignment problems.[6] 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. 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] a-Fe_2PO_5,[7] and $YBa_2Cu_3O_y$.[8] However, in a limited machine time how to obtain enough f' values without increasing refinement errors greatly is still a problem to be considered. In present work, an in-advance simulation method was introduced to copy with this problem. That method makes it possible that measurements of only a few selected reflections will be sufficient to obtain the f' curves for the specified element in two different states.

The simulation for the X-ray powder diffraction pattern can be done using the Rietan-97β software[9] if the crystal structure parameters are given. With the results of the simulation, it is possible to determine which peaks should be measured and which peaks could be skipped in experiment.

Co_3O_4 powder specimen that crystallizes in the magnetite structure was used as an example. In Co_3O_4, there exist two type of cobalt ions, Co^{2+} at the Co(1) site and Co^{3+} at Co(2) site. The simulation for this material was done using the structural parameters obtained by Roth.[10] By assuming the K edge of Co(1) is 5eV lower than the K edge of Co(2), the incident X-ray energy was set at 7.702keV to ensure that the X-ray energy is below both absorption edges of Co(1) and Co(2) as the absorption edge of Co(1) is 7.709 keV. According to the table calculated by Sasaki,[11] which is based on the Cromer and Liberian theory,[12] the anomalous scattering factors f' for Co(1) and Co(2) were -8.37 and -6.87. The patterns simulated before and after exchanging f' of Co(1) and Co(2) and their difference are shown in Figure 1

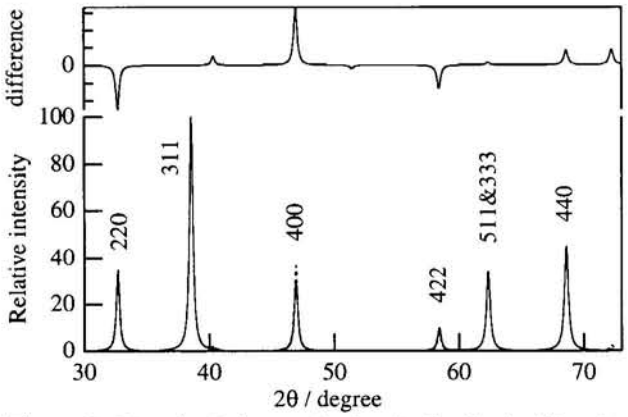

Figure 1. The simulation results for Co_3O_4. Dashed line: the edge of Co(1) is 5eV lower than Co(2); Solid line: the edge of Co(2) is 5eV lower than Co(1). Upper: the difference.

from which the peaks that are sensitive to f' can be clearly identified. Here, the two patterns were normalized at the most intensive peak (311).

Synchrotron radiation powder diffraction data collection was carried out using the powder diffractometer for synchrotron radiation with a multiple-detector system at BL4B2 of the Photon Factory in KEK. 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 simulation mentioned above, 6 peaks were chosen to be measured at 6 energy points near the absorption edge of Co. The intense peaks were preferred when considering the statistical error. The measured peaks are shown in Figure 2.

To determine the real part of anomalous scattering factors, f', for Co(1) and Co(2), the source code of Rietan-97β[9] was modified. In the analysis, we assumed that the imaginary part of the anomalous scattering factor, f", was a simple step function, the value of which was determined only by the incident X-ray energy being below or above the absorption edge. The values for f" were obtained from the table values calculated by Sasaki.[11] The determination of whether the incident X-ray energy was below or above the edge was based on the measurement of the XANES for Co_3O_4 powder.

f' and their estimated standard deviations determined from all of 6 peaks, those determined from 3 peaks (220, 311, 400) and those determined from the different set of 3 peaks(311, 511&333, 440) are shown in Figure 3, Figure 4 and Figure 5 respectively.

From the results obtained respectively from 6 peaks and 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 on the powder diffraction pattern may be

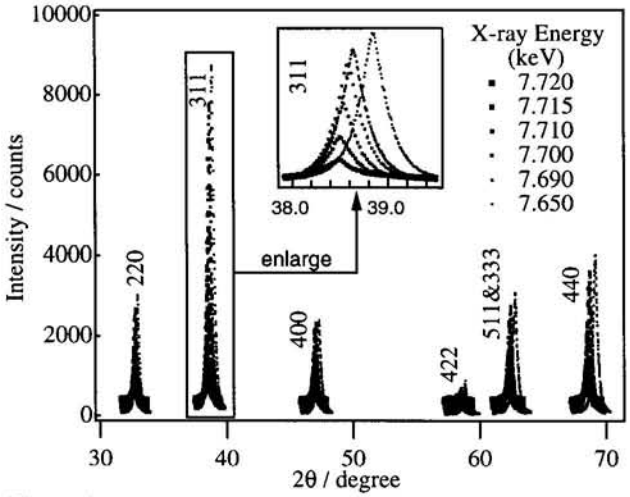

Figure 2. The collected powder diffraction peaks for Co_3O_4 at 6 energy points near the absorption edge of Co.

enough to obtain the anomalous scattering factor, f'. Here, in addition to the most intensive peak(in this work 311), we should select two more peaks that show the largest and the second largest differences in simulated pattern intensity. However, f' determined

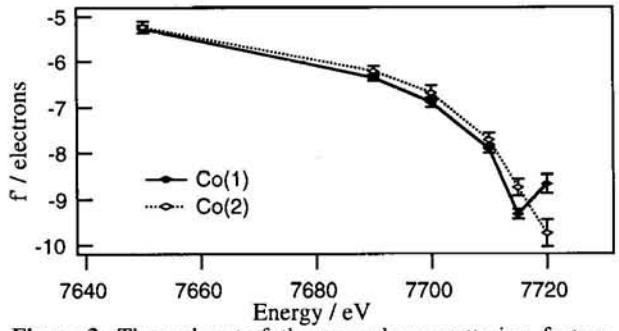

Figure 3. The real part of the anomalous scattering factors f' determined from all of 6 peaks.

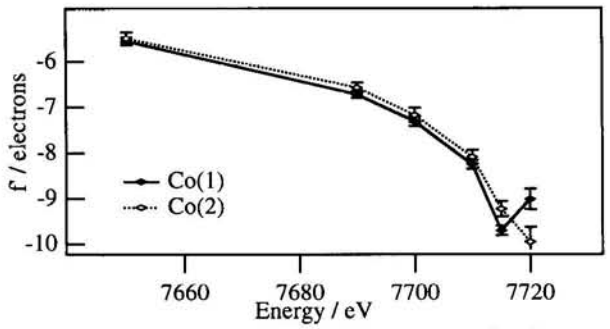

Figure 4. The real part of the anomalous scattering factors f' determined from 3 peaks (220,311,400).

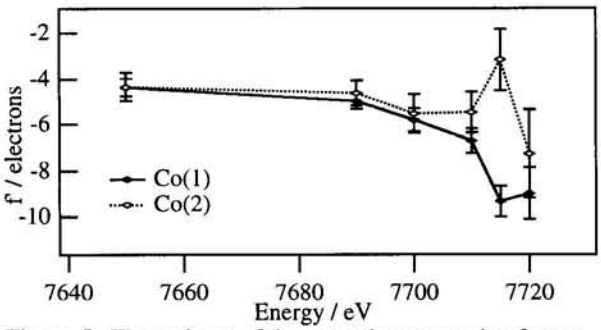

Figure 5. The real part of the anomalous scattering factors f' determined from the different set of 3 peaks (311), (511)&(333), (440).

from the different set of 3 peaks(311, 511&333, 440) came with large standard deviations. This means that how to select appropriate 3 peaks among 6 peaks is quite important. From the simulation result shown in Figure 1, it could be found that the former 3 peaks set are sensitive to the changes in the anomalous scattering factor while the later 3 peaks set are not. Thus, in order to obtain the correct f' values, it is important to select the appropriate set of three peaks.

As conclusions, there are peaks that are sensitive to and peaks that are not sensitive to the exchange of f' of the specified element at two crystallographic sites. The experiment results prove that it is possible to measure only a few peaks that are sensitive to anomalous scattering factor without increasing the refinement errors greatly and that the way of selecting peaks is important. The importance of in-advance simulation was proved. That 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 in limited machine time.

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