Chemical State Analysis by X-Ray Fluorescence Using Shifts of Iron K Absorption Edge

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Tunable monochromatic X-rays obtained from synchrotron radiation was used for the selectively induced X-ray emission spectroscopy (SIXES), which is an analytical technique with X-ray fluorescence detection and is based on the selective excitation of specific chemical species. The near edge absorption spectra of iron were measured by SIXES using an energy dispersive detection system with a Si(Li) detector. The present method, compared with the conventional transmission method, is particularly suitable for the chemical state analysis of trace systems of less than 10^{-10} g because of its high sensitivity. A mixture containing several chemical species could be analyzed within $\pm 6\%$ precision by SIXES.

Keywords Chemical state analysis, selective excitation, X-ray fluorescence, chemical shift, absorption edge, synchrotron radiation, iron

X-ray absorption edges have been investigated by the transmission method since the early days of X-ray spectroscopy.^{1,2} It is well known that the chemical environment of the element affects near edge absorption spectra, especially the relative position of absorption edges. From an analytical point of view, chemical shifts of absorption edges, which are on the order of 10 eV over a range of valence states, have been used for the chemical state analysis and are able to distinguish the specific chemical nature of each element and its environment. However, the direct absorption technique has inherent limitations of the sensitivity and the sample conditions^{2,3}, consequently restricting its analytical applications.

Since the fluorescent X-rays are emitted from the chemical species as the energy of the incident X-rays crosses the absorption edge of interest, the measurement of the chemical shifts is also expected to be achievable by the X-ray fluorescence detection. The selectively induced X-ray emission spectroscopy (SIXES), which is described in the present paper, is based on the selective excitation of specific chemical species by tunable synchrotron radiation (SR). Since X-ray fluorescence analysis using SR has significantly high sensitivity⁴⁻¹¹, SIXES is a promising analytical technique for the characterization of trace elements, and studies on thin films and surfaces. Furthermore it is expected to take a very short time, because only the vicinity of the absorption edge in the spectrum is measured. Compared with the analysis of the near

edge fine structure, the present technique is suitable for the determination of the concentrations of specific chemical species in a mixture containing several chemical states, which are often encountered in the actual analysis. Systematic changes in the position of the absorption edge are available for quantitative analysis.

The present paper shows the experimental results of the chemical state analysis of iron by SIXES. Determination of the concentration of the specific valence state in a mixture is discussed in detail. Application to the measurement of trace systems is also demonstrated.

Apparatus

The experiment was carried out using SR at the Photon Factory (PF) on beam line 4A. The experimental station is located 13 m from the source point. The apparatus used was the energy dispersive X-ray fluorescence system shown in Fig. 1, which is essentially the same as that used for the conventional trace element analyses reported previously.¹⁰

Two types of spectrometer were used to study the effect of the energy resolution of incident X-rays. One was a spectrometer with a vertical rotation axis equipped with a flat single crystal monochromator, and the other was designed with the horizontal rotation axis fitted with a channel cut crystal monochromator. Perfect silicon (111) crystals were used for both

Fig. 1 Schematic of the experimental arrangement for energy dispersive X-ray fluorescence measurement in monochromatic excitation mode. Both a horizontal axis spectrometer equipped with a channel cut crystal monochromator and a vertical axis spectrometer equipped with a flat single crystal monochromator were used: I.C., ionization chamber; D, Si(Li) detector.

spectrometers. The energy resolution of the incident beam was determined by the SR source characteristics and the height or the width of the slit at the monochromator. Since the SR source size is much smaller in the vertical direction than in the horizontal direction [designed source size (FWHM) is 0.45 mm and 4.68 mm respectively], the energy resolution of the spectrometer with the horizontal axis is higher than that with the vertical axis. From these SR source parameters, the energy resolution was estimated to be 1.5 eV and 8.8 eV at the iron absorption edge (7.111 keV) for the horizontal and vertical axes arrangement with the slit widths of 0.2 mm (vertical) and 0.25 mm (horizontal) respectively.

The energy of the incident X-rays was scanned through the absorption edge of the analyte element. Incident intensity was monitored by an ionization chamber with a 33 mm long air path. Since the irradiation area of the sample is rather small ($<1 \text{ mm}^2$), the sample is scanned during the measurement at each energy to avoid the effect of sample inhomogeneity.

The intensity of the K_α fluorescent X-rays was measured as a function of the incident energy, using a Si(Li) detector with an active area of 12 mm^2 and energy resolution of 160 eV at 5.9 keV. The detector was positioned at 90° to the incident beam in order to suppress the scattered radiation by use of the polarization of SR.¹¹ The total counting rate above the absorption edge was limited to less than 3000 cps. The electronic signal from the Si(Li) detector was processed through an amplifier and single channel analyzers, and then recorded on magnetic disks. For comparison of fluorescence detection with the conventional transmission experiment, the intensity of the transmitted X-rays was also measured by another ionization chamber placed just behind the sample. Data were normalized with the incident intensity, transformed to absorption coefficients (for transmission results), and were smoothed where necessary.

Fig. 2 Near edge absorption spectra obtained by X-ray fluorescence detection for iron metal and oxides of iron. The first inflection point of iron metal spectrum is set as zero-point of the energy, which corresponds to 7.111 keV. Scanning interval of energy was 0.4 eV, and measurements were made using a 10 s count at each energy interval to obtain a suitably small counting statistic error.

Results and Discussion

Near edge absorption spectrum

The samples chosen were metallic iron and its oxides of various oxidation states. Iron oxides were pulverized, mixed homogeneously with cellulose powder, and subsequently the pellets (13 mm diameter) were pressed at 200 kg/cm^2 and weighed. Each pellet had a mass of approximately 150 mg/cm^2 and the concentration of iron was 2.5%. Thin films of iron metal of various thickness were prepared by vacuum evaporation (deposited on thin Mylar film of $6 \mu\text{m}$ thick).

Figure 2 shows the absorption spectra of iron metal and oxides taken by X-ray fluorescence detection with the horizontal axis spectrometer. It is clearly seen that the absorption curve shifts to higher energy as the oxidation number increases. The absorption spectra include two discontinuities: the initial absorption jump (lower energy side) corresponds to the transition of the 1s-electron into an empty state of the 3d-4s band which has some p-character, and the second jump (higher energy side) corresponds to that of the 1s-electron to the 4p-level which is completely unoccupied.^{2,12} The initial absorption jump, which is a forbidden transition according to Laporte's rule, is much less pronounced for the oxides than for the metal, because the atomic wave functions are much more maintained in the oxides than in the solid metal, due to the larger distance between neighboring iron atoms.¹²

Considering such shapes of the absorption spectra, the positions of the absorption edges were defined as follows: the first inflection point of the absorption curve (at 0 eV in Fig. 2) was adopted for pure metal,

Fig. 3 Effect of the energy resolution of the monochromator on absorption spectrum. Energy resolution changes as a function of the slit width. (a), (b) and (c) show the spectra with the horizontal axis spectrometer. Vertical slit widths were 0.2 mm, 2 mm and 5 mm respectively. (d) shows a typical spectrum with the vertical axis spectrometer (0.25 mm horizontal slit).

and the mid-points for oxides and other compounds.² It may seem convenient to use only the peak of the spectrum (at about 20 eV in Fig. 2) because of the relatively higher counting rate. However, the shift of the peak position is rather small and so there is considerable uncertainty in determining the peak position because of the broad spectrum. Accordingly, for the chemical state analysis of iron, it is preferable to use the mid-point (or the first inflection point) as the position of the absorption edge.

Chemical shifts of absorption edges are dependent on the energy resolution of the spectrometer. Figure 3 shows the dependence of the iron metal absorption spectrum on the energy resolution of the incident X-rays. The fine structure became blurred as the energy resolution of the incident X-rays degraded, while the chemical shift of the absorption edge was still clearly visible. There is no problem for the analytical measurement when each spectrum is measured under the same energy resolution, although the spectra change in accordance with the incident energy resolution. Therefore, both the horizontal and vertical axes arrangement can be employed for the experiments of SIXES so long as the reference data are measured with the same energy resolution. In the subsequent study, the horizontal axis spectrometer was adopted so as to also observe the fine structure of the spectra.

Comparison with the conventional transmission experiments

Transmission experiments, which measure the absorption directly, have limitations on the sample conditions: it is extremely difficult to apply it to the

Fig. 4 Comparison of the absorption edges of various iron compounds obtained by the fluorescence and transmission methods.

analysis of thin films and dilute systems due to the restriction of the statistical errors.^{2,3,13} The optimum thickness of the sample is determined by the absorption coefficient. A uniform sample is also essential for the transmission method. Furthermore deformation of the spectrum of the rather thick sample is observed due to "thickness effects" caused by the spectral windows.¹⁴

On the contrary, the fluorescence technique is expected to be far more versatile for the sample condition, although it does not measure the absorption coefficient directly. In order to confirm the accordance between the present method and the normal transmission method, various iron compounds were measured by both techniques at the same time. Reagents of iron compounds were pulverized into fine powder and stuck onto tape, with sample loading of less than 10 mg/cm². Energies of absorption edges obtained are shown in Fig. 4. The first inflection point of the iron metal spectrum taken by the fluorescence detection was adopted as the zero of the energy. Since the energies of the absorption edges obtained from both methods were in good agreement, it is concluded that the present technique yields essentially the same results as the conventional transmission means.

However, the fluorescent X-ray intensity is no longer directly proportional to the absorption coefficient for thick or concentrated samples. Consequently, the energy dependence of the fluorescence intensity does not always agree with the absorption spectrum itself for such cases. In the extended X-ray absorption fine structure (EXAFS) region, where X-ray absorption spectra taken by X-ray fluorescence detection have been extensively studied^{13,15,16}, the effect of the thick or concentrated sample was discussed as the degradation of the sensitivity.¹⁷ The near edge spectrum is, however, probably affected by the sample condition far

Fig. 5 Dependence of the spectra obtained by fluorescence detection on thickness of the film. Solid line, broken-and-dotted line, broken-and-double-dotted line show the results of 1040 Å, 4040 Å and 1 μm film respectively. Broken line shows the transmission results of 1040 Å film.

more severely due to the drastic change of the X-ray penetration process. The position of the mid-point is expected to strongly depend on such distortion of the curve profile. Hence it is important to know more precisely about the relationship between the spectrum taken by the present method and the absorption coefficient itself.

In order to study the effect of the sample condition, thin films of iron metal of various thickness were measured. Some of the results are shown in Fig. 5. As the thickness of the film increases, the normalized absorption curve obtained by the fluorescence method moves toward the low energy side, while the transmission results remain almost constant. Good agreement between both methods was obtained for a film of less than 1040 Å thick. The result illustrated in Fig. 5 can be explained by the effect of the abrupt change of the penetration depth at the threshold. For thick samples, the effective volume contributing to the X-ray emission is reduced above the edge because of the abrupt decrease of the penetration depth of incident X-rays. As a result, the absorption edge moves toward the low energy side, which is emphasized in the normalized curve.

These effects of the sample conditions were quantitatively confirmed by theoretical calculations¹⁸, and it was found that correction of fluorescence intensity was needed and possible for a pure metal of more than a few μm thick and for a low-Z matrix sample of more than 5–6% concentration. Therefore it is concluded that we can apply SIXES not only to the thin or dilute cases, but also to the thick or concentrated cases with careful analysis. Such versatility of sample preparation may allow more applications to various practical materials.

Determination of the specific chemical species in mixture

One of the most important analytical applications of

Fig. 6(a) Near edge absorption spectra of the mixture of iron oxides by SIXES.

Fig. 6(b) Quantitative analysis of the mixture of iron oxides. Energy of the absorption edge was defined as the mid-point of the normalized absorption curve. The calibration curve given by the calculation is shown by the broken line. Open circles and cross show the raw and corrected experimental data respectively.

SIXES is the determination of the concentration of the specific chemical species in a mixture sample. In the present paper, Fe–O systems were analyzed. Figure 6(a) shows the near edge spectra of iron from mixed samples containing FeO and Fe₂O₃ in various ratios. Used samples were pellets prepared in the same way as previously mentioned, and the total iron concentration in each sample was 2.5%. The curves at the highest and the lowest energy side correspond to the spectra of pure Fe₂O₃ and FeO respectively. Since the absorption edge systematically shifts to a higher energy as the concentration of Fe₂O₃ increases, the concentration of each oxidation state can be determined using the position of the absorption edge.

Figure 6(b) shows the relationship between the chemical shift of the edge (*i.e.*, the energy of the mid-point of the curve) and the concentration of iron(III). The calculated calibration curve, which is obtained

from the syntheses of the experimental curves of pure Fe_2O_3 and FeO , is not linear, due to the differences in the shapes of the spectra for FeO and Fe_2O_3 . Determination of the mixed ratio of the unknown sample, in principle, can be performed using the calibration curve shown by the broken line in Fig. 6(b).

However, experimental results directly obtained from Fig. 6(a) do not agree with the calculated calibration curve, especially in the region of low concentration of iron(III). This is due to the particle size effect of the X-ray fluorescence intensity. Since the particle size of Fe_2O_3 (< a few μm) was smaller than that of FeO (a few tens of μm) in our case, iron fluorescent X-rays from FeO are reduced due to the absorption in the particle compared with those from Fe_2O_3 including the same quantity of iron. Therefore, careful analysis is necessary when each chemical species of a given material has a significantly different grain size. In order to know the actual ratio of the fluorescent intensities from FeO and from Fe_2O_3 at the absorption edge, we used the fluorescence intensity measured far above the absorption edge, where fluorescence intensity does not depend on the chemical states. Effect of the particle size is estimated using these data and the mixed ratios, because the total concentration of iron are the same for all samples. Hence experimental results were successfully corrected and are in good agreement with the calculated calibration curve as shown in Fig. 6(b).

The accuracy of the present method is determined by the calibration curve in Fig. 6(b); the experimental error caused by the inhomogeneity of the grain size among the species is considered also. Precision depends on the amounts of the chemical shifts, and errors in the determination of the absorption edge. The latter is mainly due to the counting statistics. Since the differences between the edge energy of FeO and Fe_2O_3 is about 3.5 eV, the chemical composition of the mixture can be determined within $\pm 6\%$ error, assuming that the absorption edge is determined within ± 0.2 eV.

Chemical state analysis of trace elements

The advantage of SIXES, compared with the conventional transmission method, lies in the significantly high sensitivity in the measurement of trace levels. Figure 7 shows the spectrum of iron (Fe^{3+}) adsorbed to resin beads (CHP20, Mitsubishi Kasei Co. Ltd.) stuck onto tape. The irradiation area was about 1 mm^2 . Sample thickness including the tape mass was 8.7 mg/cm^2 and the concentration of iron was $3.6 \times 10^{-4} \text{ g/g}$. Near edge spectrum was obtained for the element of several hundreds ppm within 15 min.

Since the mid-point for absorption edge energy is calculated by averaging the counts of the peak (N_H) and the background (N_L), its precision depends on the counting statistics of both N_H and N_L . While N_H is mainly from the analyte element, N_L is the background mainly due to scattered radiation, especially for

Fig. 7 Spectrum of iron(III) adsorbed to resin beads stuck onto tape. The detector solid angle ($\Omega/4\pi$) is 9.3×10^{-4} .

samples composed of low-Z matrices. It is therefore important to eliminate scattered radiation for the measurements of trace systems. Though a Si(Li) detector was used to separate scattered radiation from the fluorescence signal in the present case, the effect of scattered radiation could not be perfectly eliminated.

Fluorescent X-rays emitted from major elements also restrict the measurement of trace species by saturating the counting rate of the detector. For example, chemical state analysis of iron at trace level is often limited by the strong fluorescence flux emitted from the major components of lower-Z elements. Even if the absorption edge energy of the major element is higher than that of the trace element of interest, higher order harmonics of the incident X-rays sometimes affect the measurement in the same way.

The sensitivity limit under the present condition was estimated by taking into account the errors in the determination of the absorption edge. On the assumption that the absorption edge is determined by the direct comparison of the spectrum of the trace species with that of the same species obtained with sufficient counting statistics, the fluctuation of the absorption edge ΔE can be written as follows:

$$\Delta E = \pm \frac{1}{A} \left(\frac{\sqrt{N_L}}{N_H - N_L} + \frac{\sqrt{N_H + N_L}}{2(N_H - N_L)} \right) \dots \dots \dots (1)$$

where A represents the slope of the absorption curve. The former and the latter terms in Eq. (1) correspond to the fluctuation just below the edge and the error in the determination of the mid-point respectively. With the present detection system, for 100 ppm iron in 7 mg/cm^2 low-Z matrix sample, the fluorescence intensity above the edge and the background with 1 mm^2 irradiation area are ca. 1500 counts/s and a few tens counts/s respectively. The minimum signal counts, which are necessary for the determination of the edge energy of the normalized absorption curve of 0.07/eV slope within ± 1 eV by 5 min measurement, are estimated

using Eq. (1). The calculation shows that chemical states of iron in the order of ppm or 10^{-10} g in low-Z matrices are analyzed. For a thin film of iron metal, exhibiting very weak background intensity of scattered radiation, less than 0.1 monolayer (in the order of 10^{11} atoms) is the sensitivity limit under the same conditions. It is extremely difficult to study these trace systems and thin films by any other technique.

In conclusion, the high photon flux of tunable monochromatic X-rays from SR makes possible the chemical state analysis of trace elements by SIXES. The determination of specific chemical species in a mixture was performed by measuring the absorption edge shifts. The advantages of the measurement of the near edge absorption spectrum by SIXES over that by the transmission technique are summarized as follows: (i) Since it has high sensitivity, it can be used for trace element analysis, in the order of ppm or 10^{-10} g. (ii) It can also be used with thin films and surfaces. Some results of the characterization of thin films are presented elsewhere.¹⁹ SIXES is a promising tool for the characterization of industrial and biomedical materials because of its nondestructive nature and versatility as regards the environment required for the measurement and the form of samples.

Another important application of SIXES is the investigation of the spatial distribution of specific chemical species in a complex mixture, tuning the incident energy. For example, the fluorescence intensity from Fe_2O_3 is far lower than that from FeO at a certain energy near the edge, while both FeO and Fe_2O_3 are excited above the edge. From these measurements, the spatial distribution of each chemical species is determined independently. These results will be published elsewhere.²⁰ Such chemical information also cannot be obtained so easily by any other technique.

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