CHEMICAL STATE ANALYSIS BY X-RAY FLUORESCENCE

USING ABSORPTION EDGES SHIFTS

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INTRODUCTION

Recently synchrotron radiation (SR) sources have been extensively used for the study of materials science.[1,2] The high intensity of tunable monochromatic X-rays from SR facilitates many types of spectroscopic/ diffraction studies which have otherwise not been possible. Regarding the X-ray fluorescence technique, significant improvement of the minimum detection limit has been performed and has enabled trace element analysis in the order of tens of ppb or 10^{-12} g.[3-8] SR microanalyzers[3,9,10] and near surface analysis using grazing incidence geometry[11,12] are also attractive applications of synchrotron X-ray fluorescence technique. From a point of materials characterization, chemical state analysis is not less important than ordinary element analysis.

The selectively induced X-ray emission spectroscopy (SIXES)[13-16], which is based on the selective excitation of specific chemical species by tunable SR, has recently been realized. This technique uses the chemical shifts of the absorption edges, which reflect systematic changes of the binding energies of inner shell electrons corresponding to the chemical environment. High sensitivity is one of the most important advantages of SIXES. It is significant for practical analysis because sensitive methods for chemical state analysis are extremely limited.

In this paper, chemical state analysis by SIXES is described, with emphasis on the quantitative analysis of the mixed system and also on chemical state mapping.

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PRINCIPLE OF SIXES

The energy of the absorption edge is the minimum energy necessary to excite the inner shell electron to the outer empty level, and shifts slightly with change of chemical environment. Since the fluorescent X-rays are emitted accompanied with the excitation of inner shell electrons, chemical shifts of the absorption edge lead to the differences in the threshold energy of the X-ray emission along the chemical species. This means that distinction of chemical states is possible with the measurement of X-ray fluorescence selectively emitted by tuning the incident energy. This is the reason why we call the present technique selectively induced X-ray emission spectroscopy (SIXES).

Chemical shifts of the absorption edges have been measured mainly by the transmission technique since the early days of X-ray spectroscopy.[17,18] The direct transmission method, however, has inherent limitations of the sensitivity and the sample conditions[18,19], consequently restricting its analytical applications. On the contrary, the absorption spectroscopy by X-ray fluorescence detection is expected to be suitable for the characterization of thin or dilute systems because of its high sensitivity. This procedure has become available since the advent of SR sources, and is employed mostly for EXAFS experiments.[20-23] The present study was designed to realize chemical state analysis with X-ray fluorescence by the observation of the systematic shifts of absorption edges.

With respect to chemical state analysis by SIXES, there are largely two types of experiments: (i) direct evaluation of the amount of chemical shift by measuring the energy dependence of the intensity of fluorescent X-rays, which gives the near-edge absorption spectrum, (ii) observation of the change or distribution of specific chemical species by measuring the dependence of fluorescent X-ray intensity on experimental parameters such as position of the sample, temperature, pressure or process of chemical reaction. In the present work, as examples for (i) and (ii), the quantitative analysis of the mixed system and chemical-state mapping are demonstrated, respectively.

EXPERIMENTAL

The experiment was carried out using SR at the Photon Factory (PF) on beam lines 4A and 6B. The apparatus used was the energy dispersive X-ray fluorescence system.[11] SR beams were monochromatized by a channel-cut Si(111) crystal monochromator. The intensity of Kα fluorescent X-rays was measured by a Si(Li) detector as a function of the incident energy, which was scanned around the absorption edge. Intensities of incident and transmitted X-rays are measured by ionization chambers. Other experimental details were described elsewhere.

NEAR EDGE ABSORPTION SPECTRUM

Figure 1 shows the near edge absorption spectra of some 3d-transition metals and their oxides. The samples were prepared in the form of pellets mixed homogeneously with fine cellulose powder.[13] The first inflection point of each metal spectrum is set at zero. It is clearly seen that the absorption curve shifts to higher energy as the oxidation number increases. The energy resolution of the incident X-rays is less than 2 eV and is sufficient to reveal shifts of the absorption edge.

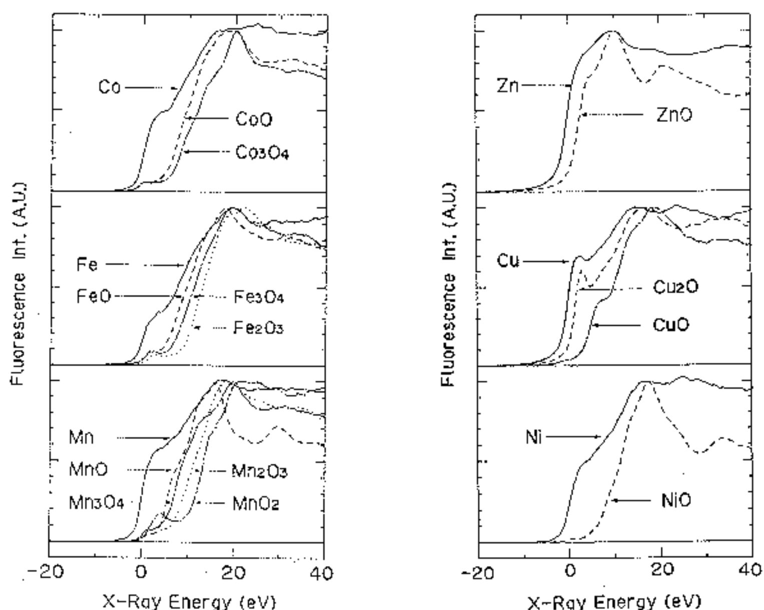

Fig. 1 Near edge absorption spectra of 3d transition metal oxides obtained by X-ray fluorescence detection.

The absorption spectra shown in Fig. 1 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 1s → 4p-level which is completely unoccupied.[18] 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. These explanations seem appropriate except for oxides of copper from Fig. 1. Pre-edge structures of copper oxides are interpreted as a split of 1s → 4p transition to 1s → 4pσ and 1s → 4pπ.[24] It is important to analyze such fine structures and complicated shapes of the spectra. From an analytical point of view, however, chemical shifts are most conspicuous and feasible features appear in the experimental spectra as shown in Fig. 1.

A comparison between the present technique and the transmission experiments is summarized in Table 1. Near-edge absorption spectra obtained from both methods were in good agreement. However, transmission experiments, which measure absorption directly, have limitations with respect to sensitivity and sample conditions: application to the analysis of thin films and dilute systems is difficult due to the restriction of the statistical errors. The optimum thickness for maximum contrast of X-ray intensity is usually of the order of μm. An uniform sample is also essential for the transmission method; on the contrary, with the present technique, much higher sensitivity is attainable. Trace systems in the order of ppm and thin films of less than 0.1 monolayer can be analyzed by SIXES.[13,15] Furthermore, it is far more versatile for sample conditions than is the direct absorption technique. Though distortion of the spectra is observed for concentrated or

Table 1. Comparison of Transmission and Fluorescence Methods

	Transmission Technique	Fluorescence Technique (SIXES)
Analytical Information	essentially the same	
Sensitivity	optimum thickness ∿μm	∿ppm; less than ng
Inhomogeneous Sample	not suitable	suitable

thick samples, the position of the absorption edge can be determined using reference spectra.[14]

DETERMINATION OF THE CHEMICAL COMPOSITION OF MIXTURES

The determination of the chemical composition of a mixed system is one of the most interesting analytical applications of SIXES. Figure 2 shows the near-edge spectra from mixed samples containing FeO and Fe_2O_3 in various ratios. The absorption edge systematically shifts to the higher energy side as the concentration of Fe_2O_3 increases. The concentration of each oxidation state can be determined by the position of the absoprtion edge. The calibration curve, which is obtained experimentally using reference samples by plotting the edge energy as a function of the ratio of the components, was used for quantitative analysis. The precision of the present method was found to be about ± 6%.[13]

As an example of the practical application of SIXES, thin Co-O films which show perpendicular magnetic properties were analyzed.[15] According to the recent studies,[25,26] thin films of Co-O are expected to be composed of

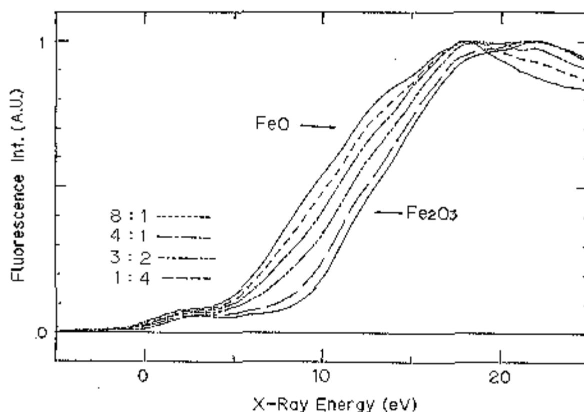

Fig. 2 Quantitative analysis of mixtures of iron oxides

Table 2 Preparation Conditions of Co-O Thin Films

	O content	Magnetism	Color
A	———	magnetic	metallic
B	↓ increasing		black
C			
	- - - - - - - - - -		
D	critical pressure	non-magnetic	colorless transparent
	- - - - - - - - - -		
E	↓		

ferromagnetic cobalt metal and non-ferromagnetic CoO below a critical pressure. However, it is sometimes difficult to analyze these films by X-ray crystal structural analysis, because very fine particles of cobalt metal are surrounded by the layer of CoO in the Co-O film.[25,26]

The preparation conditions of Co-O thin films are listed in Table 2. They were prepared by vacuum evaporation with an electron beam gun and deposited on thin polyimide films. Oxygen gas was introduced during the cobalt evaporation, at a rate of approximately 1600 Å/sec, at various pressures ($4 \times 10^{-4} \sim 1 \times 10^{-3}$ Torr), and oxygen content was gradually increased for samples A through E. Sample D was prepared at the critical pressure, where saturation magnetization of the film became zero. The cobalt absolute mass of the films was about 200 $\mu g/cm_2$ ($\sim$2000 Å). Sample E was prepared by drastically lowering the cobalt evaporation rate, and contains an extremely high proportion of oxygen.

The experimental results for thin Co-O films are shown in Fig. 3. Absorption edges shift to the higher energy side as the oxygen pressure increases. These spectra were analyzed by direct comparison with the

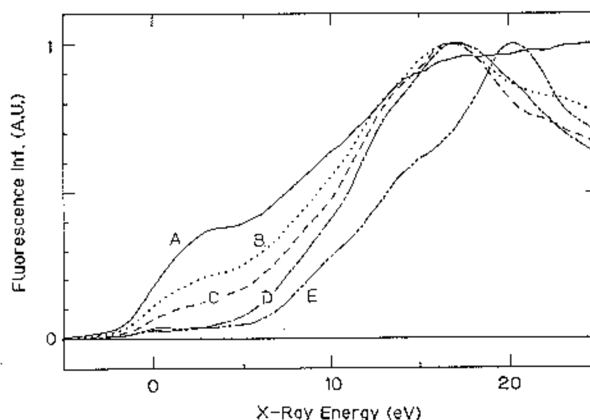

Fig. 3 The absorption spectrum for Co-O thin films. Partial pressure of oxygen was increased in the order A (solid line), B (dotted line), C (broken line), D (broken-and-dotted line), E (broken-and-double-dotted line).

reference spectra of cobalt oxides as shown in Fig. 1. As a result, curves A, D and E are in good agreement with the spectra of cobalt metal, CoO and Co_3O_4, respectively. Curves B and C correspond to the mixture of cobalt metal and CoO. The results show a gradual change in the Co-O films from pure cobalt metal into CoO through the mixed state of cobalt metal and CoO. Furthermore Co-O films become Co_3O_4 above the critical oxygen pressure. The ratios of cobalt metal to CoO in mixtures can also be determined; they were about 1 to 1 and 3 to 7 for samples B and C, respectively.

Accordingly, it was demonstrated that SIXES can be applied to the analysis of thin films even when there is no long range order suited for using ordinary X-ray diffraction techniques. Capability of quantitative treatment is its most important feature.

CHEMICAL STATE MAPPING

Chemical state mapping is another important analytical application of SIXES.[16] Such a technique, especially with high sensitivity, has hardly been developed yet in practice, in spite of increasing demands in scientific studies. The absorption imaging technique,[27] which is promising for three dimensional imaging in combination with X-ray computed tomography, is severely restricted with respect to sensitivity.

At the lower energy side of the absorption edge (0 ∿ 10 eV in Fig.1) excitation efficiency differs considerably among the chemical species. The intensities of fluorescent X-rays of lower oxidation states are more intense than those of higher oxidation states for the same quantity. This means that information of specific chemical species can be separated from others, though it is difficult to realize perfect selective exictation. On the contrary, excitation efficiency is almost the same at the higher energy side of the absorption edge (above 20 eV in Fig.1), in the same way as the ordinary element analysis with fluorescent measurement.

The intensity of fluorescent X-rays from a specific chemical species is proportional to the product of its concentration and its excitation efficiency. The observed intensity at the incident excitation energy E_j can be written as follows:

$$I(E_j) = A \cdot \sum_{i=1}^{n} F_i(E_j) \cdot C_i \qquad (1)$$

where C_i and $F_i(E_j)$ are the concentration of the chemical state i and the excitation efficiency of i and E_j, respectively; n is the number of chemical states contained in the sample and A is a constant. Using Eq.(1), C_1, C_2, $\cdots$, C_n are determined when $I(E_1)$, $I(E_2)$, $\cdots$, $I(E_n)$ are given experimentally. For example, in the case of a binary system, for the determination of each concentration, it is necessary to measure the fluorescent intensity at two energies.

For an experiment on chemical state mapping, a pellet sample having separated regions of FeO and Fe_2O_3, was studied.[16] The intensity distribution of Fe Kα was measured by point-by-point scanning with a beam size of 250 μm x 500 μm. The measurements were performed at the lower (8.1 eV in Fig.1) and higher energy sides (20.0 eV in Fig.1) of the absorption edge with pixels of 100 x 20 points, and the collection time was 2 sec for each pixel. The sample was scanned from the FeO region through the Fe_2O_3 region.

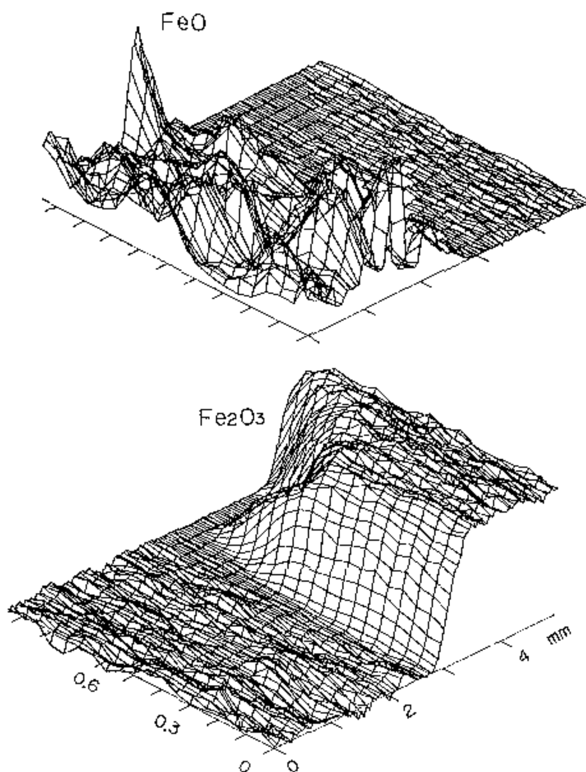

Fig. 4 Chemical state mapping of the iron oxide sample by SIXES.

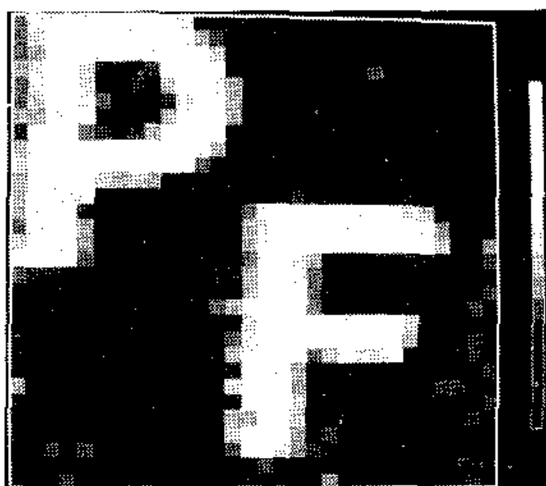

Fig. 5 Chemical state mapping (Cr image). The Cr_2O_3 image obtained was a reversal of the Cr image.

By substituting the experimental intensity distribution of Fe Kα data in Eq.(1), the spatial distributions of FeO and Fe_2O_3 were determined separately as shown in Fig. 4. The results were in good agreement with the distributions obtained by an optical microscope. The concentration of FeO has many peaks because of an inhomogeneous distribution of relatively large size particles of a few hundreds μm in diamter, whereas the fine powders of Fe_2O_3 are distributed almost uniformly.

Another example is given in Fig. 5. The sample is a thin film of chromium on glass. Letters of 'PF' are chromium metal, and chromium oxide Cr_2O_3 is deposited around them. Figure 5 shows the mapping of chromium metal which is in good agreement with the optical image.

Though focusing optics was not used in the present work, it is very attractive for providing high resolution imaging with an SR microprobe[9,10] having a μm-order resolution. Microstructures of various materials will be analyzed more clearly by investigating the chemical state of the specific element. Application of the image reconstruction technique is also important.[16,28] This experiment is performed using a line beam with translational and rotational scannings of the sample, and is superior in getting a high counting rate of the signal as a result of a relatively larger irradiation area. Since the SR beam has an inherent line shape, high-resolution imaging with X-ray demagnification optics is feasible.[28] The present technique indicates possible new developments in extensive scientific fields, considering its nondestructive nature and versatility in regard to the requirements of measurement and the form of the sample.

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REFERENCES

1. H. Winick and S. Doniach Eds., "Synchrotron Radiation Research", Plenum, New York (1980).
2. E. E. Koch Ed., "Handbook on Synchrotron Radiation", North-Holland, Amsterdam (1983)
3. C. J. Sparks, Jr., X-Ray Fluorescence Microprobe for Chemical Analysis, in "Synchrotron Radiation Research", Ch. 14, H. Winick and S. Doniach Eds., Plenum, New York (1980)
4. J. V. Gilfrich, E. F. Skelton, D. J. Nagel, A. W. Webb, S. B. Qadri and J. P. Kirkland, X-Ray Fluorescence Analysis Using Synchrotron Radiation, Adv. in X-Ray Anal. 26:313 (1983)
5. R. D. Giauque, J. M. Jaklevic and A. C. Thompson, The Application of Tunable Monochromatic Synchrotron Radiation to the Quantitative Determination of Trace Elements, Adv. in X-Ray Anal. 28:53 (1985).
6. S. T. Davies, D. K. Bowen, M. Prins and A. J. J. Bos, Trace Element Analysis by Synchrotron Radiation Excited XRF, Adv. in X-Ray Anal. 27:557 (1984)

7. A. Iida, K. Sakurai, T. Matsushita and Y. Gohshi, Energy Dispersive X-Ray Fluorescence Analysis with Synchrotron Radiation, Nucl. Instr. and Methods 228:556 (1985)
8. K. Sakurai, A. Iida and Y. Gohshi, Analysis of Signal to Background Ratio in Synchrotron Radiation X-Ray Fluorescence, Anal. Sci. 4:3 (1988)
9. R. D. Giauque, A. C. Thompson, J. H. Underwood, Y. Wu, K. W. Jones, M. L. Rivers, Measurement of Femtogram Quantities of Trace Elements Using an X-ray Microprobe, Anal. Chem. 60:855 (1988)
10. Y. Gohshi, S. Aoki, A. Iida, S. Hayakawa, H. Yamaji and K. Sakurai, A Scanning X-Ray Fluorescence Microprobe with Synchrotron Radiation, Adv. in X-Ray Anal. 31:495 (1988)
11. A. Iida, K. Sakurai, and Y. Gohshi, Grazing Incidence X-Ray Fluorescence Analysis, Nucl. Instr. and Methods A246:736 (1986)
12. A. Iida, K. Sakurai, and Y. Gohshi, Near-Surface Analysis of Semiconductor Using Grazing Incidence X-Ray Fluorescence, Adv. in X-Ray Anal. 31:487 (1988)
13. K. Sakurai, A. Iida and Y. Gohshi, Chemical State Analysis by X-Ray Fluorescence Using Shifts Of Iron K Absorption Edge, Anal. Sci. 4:37 (1988)
14. K. Sakurai, A. Iida and Y. Gohshi, Chemical State Analysis of Trace Elements by X-Ray Fluorescence Using Absorption Edge Shifts, Adv. in X-Ray Chem. Anal. Japan 19:57 (1988) [in Japanese]
15. K. Sakurai, A. Iida and Y. Gohshi, Characterization of Co-O Thin Films by X-Ray Fluorescence Using Chemical Shifts of Absorption Edges, Jpn. J. Appl. Phys. 26:1937 (1987)
16. K. Sakurai, A. Iida, M. Takahashi and Y. Gohshi, Chemical State Mapping by X-Ray Fluorescence Using Absorption Edge Shifts, to be published in Jpn. J. Appl. Phys.
17 L. V. Azaroff and D. M. Pease, in "X-ray Spectrometry", Ch. 6, L. V. Azaroff, Ed., McGraw-Hill, New York (1974)
18. B. K. Agarwal, "X-ray Spectroscopy", Springer-Verlag, New York (1979)
19. M. E. Rose and M. M. Shapiro, Statistical Error in Absorption Experiments, Phys. Rev. 74:1853 (1948)
20. J. M. Jaklevic, J. A. Kirby, M. P. Klein, A. S. Robrtson, G. S. Brown and P. Eisenberger, Fluorescence Detection of EXAFS: Sensitivity Enhancement for Dilute Species and Thin Films, Sol. Stat. Commu. 23:679 (1977)
21. J. M. Jaklevic, J. A. Kirby, A. J. Ramponi, and A. C. Thompson, Chemical Characterization of Air Particulate Samples Using X-ray Absorption Spectroscopy, Environ. Sci. Technol. 14:437 (1980)
22. E. A. Stern, and S. M. Heald, in "Handbook on Synchrotron Radiation", Ch. 10, E. E. Koch Ed., North-Holland, Amsterdam (1983)
23. H. Oyanagi, T. Matsushita, H. Tanoue, T. Ishiguro and K. Kohra, Fluorescence-Detected X-Ray Absorption Spectroscopy Applied to Structural Characterization of Very Thin Films: Ion-Beam-Induced Modification of Thin Ni Layers on Si(100), Jpn. J. Appl. Phys. 24:610 (1985)
24. N. Kosugi, XANES and Molecular Orbital Picture: 3d Transition Metal Compounds, in "Core Level Spectroscopy in Condensed Systems", A. Kotani Ed., Springer-Verlag (1988)
25. K. Nakamura, N. Tani, M. Ishikawa, T. Yamada, Y. Ota and A. Itoh, A New Perpendicular Magnetic Film of Co-O by Evaporation, Jpn. J. Appl. Phys. 23:L397 (1984)
26. M. Ohkoshi, K. Tamari, S. Honda and T. Kusuda, Microstructure and exchange anisotrophy of Co-CoO films with perpendicular magnetization, J. Appl. Phys. 57:4034 (1985)

27. J. Kinney, Q. Johnson, M. C. Nichols. U. Bonse and R. Nusshardt, Elemental and Chemical-State Imaging Using Synchrotron Radiation, Appl. Opt. 25:4583 (1986)
28. A. Iida, M. Takahashi, K. Sakurai and Y. Gohshi, SR X-Ray Fluorescence Imaging by Image Reconstruction Technique, to be published in Rev. Sci. Instrum.