

## Micro-XANES by EPMA spectrometer

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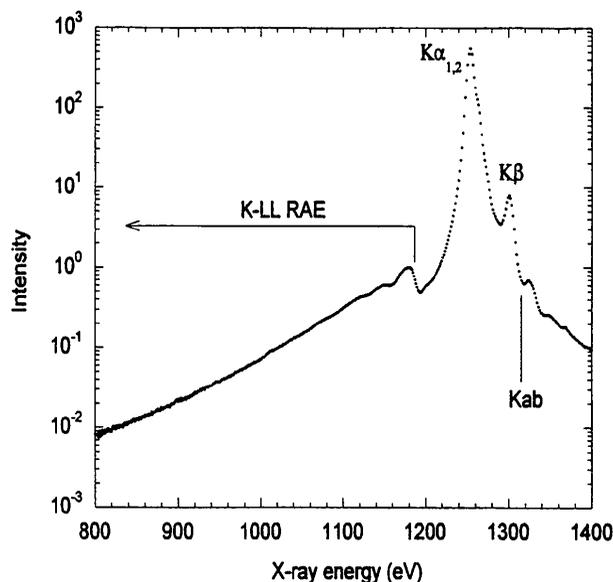
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XANES (X-ray absorption near edge structure) spectrum of an area of a few tens of square micrometers of MgO is measured with an EPMA (electron probe X-ray microanalyzer) using a novel method -- EXEFS (extended X-ray emission fine structure) method -- proposed by the present authors. The EXEFS method has the following six remarkable characteristics: (1) high energy resolution, (2) high spatial resolution, (3) short measuring time, (4) easy sample preparation, (5) convenient without using synchrotron radiation facilities, and (6) good at measuring soft X-ray absorption spectra.

**Keywords:** X-ray emission spectroscopy; electron probe X-ray microanalyzer; EPMA; radiative Auger effect; EXEFS

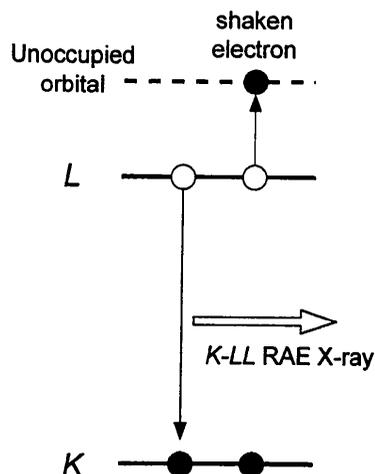
Strong characteristic X-ray lines are accompanied by weak lines due to the radiative Auger effect (RAE) (Åberg, 1971). In the present paper, we demonstrate that the profiles of the RAE X-ray emission spectra measured by an electron probe X-ray microanalyzer (EPMA) resemble those of the X-ray absorption near edge structure (XANES) spectra. We proposed to call this EXEFS (abbreviation of Extended X-ray Emission Fine Structure) (Kawai *et al.*, 1998*a*, 1998*b*). A square micrometer area XANES and EXAFS spectroscopy can be performed because the electron probe size of an EPMA is as small as 1  $\mu\text{m}$  diameter.

Figure 1 shows a representative Mg  $K\alpha$  X-ray fluorescence spectrum, in which the  $K$ -LL RAE fine structures are found on the low energy tail of the  $K\alpha$  main line. This low energy structure is due to the energy loss at the moment of X-ray emission as is illustrated in Fig. 2. The characteristic  $K\alpha$  X-rays



**Figure 1**

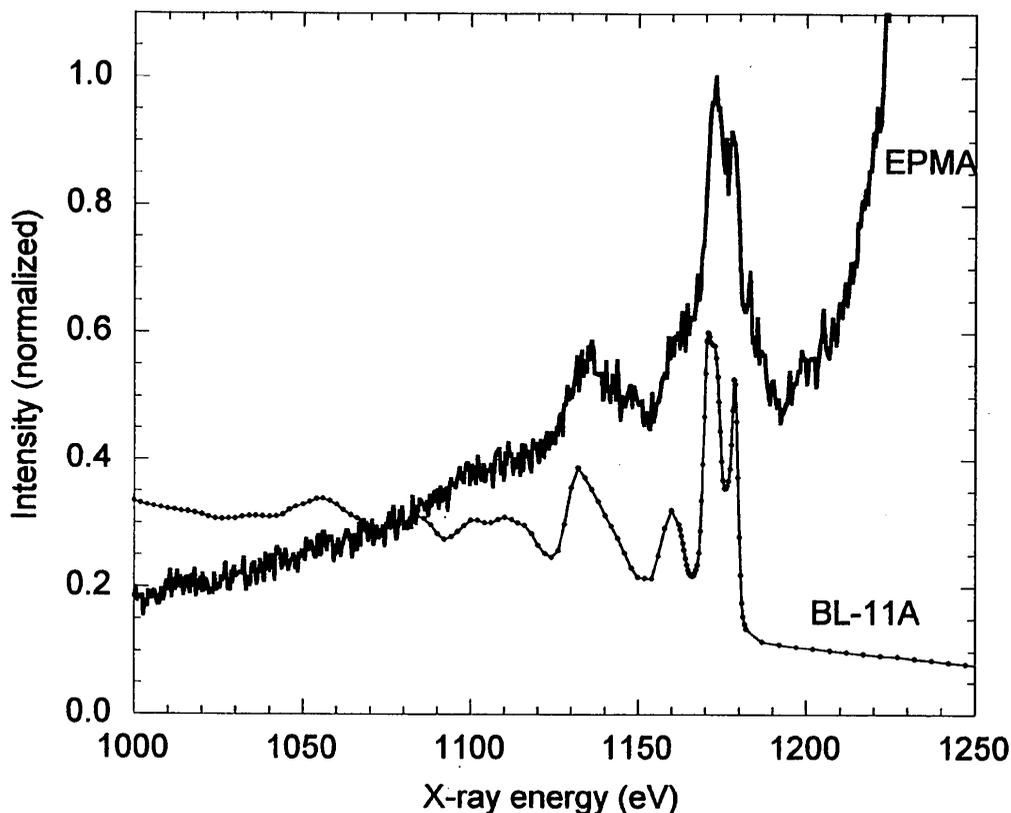
A representative  $K\alpha$  X-ray emission spectra of metallic Mg.  $K_{ab}$ : absorption edge. This spectrum was measured by a low resolution wavelength dispersive X-ray fluorescence spectrometer. The EPMA spectra are obtainable with higher energy resolution, because EPMA uses a curved X-ray crystal.



**Figure 2**

Schematic energy level diagram of  $K$ -LL RAE X-ray emission.

( $K$ - $L_{2,3}$  lines) are emitted by the  $2p \rightarrow 1s$  electric dipole transition. Though the probability is very low, one of the  $2p$  electrons is excited into an unoccupied discrete or continuum level simultaneously with the  $K\alpha$  X-ray emission, because of an effect of the sudden change of the atomic potential before and after the  $2p \rightarrow 1s$  electric dipole transition. This many body effect is called the radiative Auger effect. The shaken electron cannot change the orbital angular momentum when it moves from



**Figure 3**  
Measured MgO EPMA spectra compared with synchrotron radiation XANES (BL-11A).

$2p$  to an unoccupied orbital (monopole selection rule). Thus the unoccupied orbital should have the  $p$  symmetry. The shake probability, *i.e.* the RAE spectral intensity, is crudely proportional to the  $p$  state density of the unoccupied level. This is similar to the  $1s$  X-ray absorption fine structure (XAFS).

We have measured the MgO EPMA spectra using a JEOL Super Probe JXA-8800R with the electron acceleration potential 15 kV and the electron beam current 0.2  $\mu\text{A}$ . The beam diameter was 40  $\mu\text{m}$ , and the analyzing crystal was Johan type TAP (thallium acid phthalate). Dwelling time for one channel was 1 s from 962 to 1236 eV with 620 channels. Twenty iterations were accumulated and plotted in Fig. 3. The vacuum was  $10^{-3}$  Pa.

To compare the EXEFS spectra with genuine XANES spectra, XANES spectrum of MgO was measured at the beam line BL-11A (Kitajima, 1996, 1997, 1998*a*, and 1998*b*) at the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. The 2.5 GeV storage ring current was operated at 300-250 mA during measurement. Beam size was 2 mm  $\times$  0.5 mm. Incident monochromated beam intensity ( $I_0$ ) was monitored by a gold-

coated tungsten mesh inserted in the beam line and the drain electric current was measured. The vacuum was evacuated to  $10^{-6}$  Pa. One channel was 5 or 10 s depending on the energy range. The result of one scan is plotted in Fig. 3 after normalized with respect to  $I_0$ . The XANES spectral energy in Fig. 3 was converted by a relation,  $E = 2487 \text{ eV} - E_{\text{synch}}$ , where  $E_{\text{synch}}$  was the beam line monochromator energy,  $E$  was the plotted energy, and 2487 eV was the sum of EXAFS white line energy and corresponding EXEFS peak energy.

It is striking that these two spectra resemble each other. Fine structures in the XANES spectrum was well reproduced by the EPMA EXEFS spectrum. This EPMA is the spectrum of 40  $\mu\text{m}$  diameter area. Thus we could measure  $\mu\text{XANES}$ -like spectra.

EXEFS-related works are as follows. Kawai *et al.* (1992) pointed out that the profiles of the RAE X-ray fluorescence spectra resembled to that of the X-ray absorption edge, and Hayashi *et al.* (1997) and Kawai *et al.* (1997) performed the extended X-ray absorption fine structure spectroscopy of aluminum metal and oxides by the Fourier transform of the X-ray fluorescence spectra. Tanuma *et al.* (1998) demonstrated that the EXAFS-like oscillation was observable in Al EPMA spectra

of 1  $\mu\text{m}$  diameter area. The present authors reported Si *K*-edge XANES of Si and compounds measured by the present method (Kawai *et al.*, 1998c, 1998d, 1998e, 1999a). Especially the report of Kawai *et al.* (1999b) was the XANES-like spectra of Si compounds of 1  $\mu\text{m}^2$ .

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## References

- Åberg, T. (1971). *Phys. Rev.* **A4**, 1735-1740.
- Hayashi, K., Kawai, J., & Awakura, Y. (1997). *Spectrochim. Acta*, **B52**, 2169-2172.
- Kawai, J., Nakajima, T., Inoue, T., Adachi, H., Yamaguchi, M., Maeda, K., & Yabuki, S. (1994). *Analyst*, **119**, 601-603.
- Kawai, J., Hayashi, K., & Awakura, Y. (1997). *J. Phys. Soc. Jpn.* **66**, 3337-3340.
- Kawai, J., Hayashi, K., & Tanuma S. (1998a). *Analyst*, **123**, 617-619.
- Kawai, J. & Hayashi, K. (1998b). *J. Electron Spectrosc. Relat. Phenom.* **92**, 243-245.
- Kawai, J., Hayashi, K., Okuda, K., & Nisawa, A. (1998c). *Chem. Lett.* 245-246.
- Kawai, J., Hayashi, K., Okuda, K., & Nisawa A. (1998d). *RIGAKU-DENKI Journal*, **29** (1), 23-27.
- Kawai, J., Hayashi, K., Okuda, K., & Nisawa, A. (1998e). *RIGAKU Journal*, **15** (2), 33-37.
- Kawai, J., Takahashi, H., & Shimizu, R. (1999a). *J. Trace Microprobe Technol.* **17** (1). In the press.
- Kawai, J. & Takahashi, H. (1999b). *Spectrochim. Acta*, **B54** (1) In the press.
- Kitajima, Y. (1996). *Photon Factory News*, **14** (2), 8-10.
- Kitajima, Y. (1997). *Photon Factory News*, **15** (1), 13-14.
- Kitajima, Y. (1998a). *Photon Factory News*, **16** (4), 10.
- Kitajima, Y., Amemiya, K., Yonamoto, Y., Ohta, T., Kikuchi, T., Kosuge, T., Toyoshima, A., & Ito, K. (1998b). *J. Synchrotron Rad.*, **5**, 729-731.
- Tanuma, S., & Nishio, M. (1998). *Spectrochim. Acta*, **B53**, 505-507.

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