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著者	Tohji Kazuyuki, Udagawa Yasuo, Kawasaki Tsutomu, Mieno Kimitoshi
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Double-crystal spectrometer for laboratory EXAFS spectroscopy

Kazuyuki Tohji and Yasuo Udagawa

Institute for Molecular Science, Okazaki, Aichi 444, Japan

Tsutomu Kawasaki and Kimitoshi Mieno

Rigaku Denki Co., Akishima, Tokyo 196, Japan

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A double-crystal x-ray spectrometer designed for in-laboratory EXAFS (extended x-ray absorption fine structure) study is described. By the use of two curved crystals with different structure factors such as Ge(220) and Ge(111), reflections other than the desired order are virtually eliminated and monochromatic as well as intense x-ray flux can be obtained by applying higher voltage to the x-ray generator. As a result, data of very high quality can be collected in a short period by measuring the incident and the transmitted beam intensity simultaneously. It can cover a wide spectral range (7–26 keV) and is especially useful in the high-energy region, where the laboratory EXAFS system previously reported has some difficulties.

INTRODUCTION

Extended x-ray absorption fine structure (EXAFS) is now established as one of the standard techniques of structure analysis.[1] The local geometric structure around selected types of atoms can be determined by EXAFS regardless of the phase of the substance. It is particularly useful for the structural study of the materials which lack long-range order. Inhomogeneous catalysts which consist of finely dispersed metal clusters on high area supports and biological molecules which are not available as a single crystal are typical examples. The amplitudes of EXAFS oscillations are very small compared with the total absorption background, being about 10% in the pure element to less than 1% in dilute systems. Therefore, in order to draw sound conclusions from the EXAFS analysis, measurements of very accurate absorption coefficient are prerequisite over an energy range of about 1 keV above the absorption edge.

Synchrotron radiation (SR) is the most suitable x-ray source for EXAFS measurement because of its intense photon flux, structureless spectrum, small beam divergence, and polarization. Now EXAFS spectra are routinely obtained at stations of every SR facility. In spite of its unrivaled advantages, however, use of a large facility like SR imposes some restrictions on the users. For instance, SR is not immediately accessible for the majority of workers when one gets an idea with EXAFS spectroscopy. For some kinds of studies it is crucial to have a spectrometer close to the place where samples are prepared.

Under these circumstances a great deal of effort has been devoted to develop an EXAFS spectrometer in a laboratory.[2–14] The past two methods have proposed to make full use of relatively weak x rays from conventional sources; use of a curved monochromator crystal to collect photon flux over large solid angles,[2–12] and use of position-sensitive detectors which make simultaneous measurement at many data points possible,[13,14] the former being more successful so far.

In the previous publications we have reported an EXAFS spectrometer with Johansson cut and bent crystal[9] and studied a number of catalyst structures by the use of the apparatus.[15–18] Similar systems have been described also by Khalid *et al.*,[6] Thulke *et al.*,[8] and Kampers *et al.*[10] In all these systems the incident beam intensity I_0 is measured by a semitransmitting ionization chamber simultaneously with the transmitted photon flux I, in order to compensate the fluctuation of the x-ray source. A problem inherent to the method is the contamination of undesired reflections from the crystal, if one tries to raise the accelerating voltage of the x-ray generator to increase photon flux, or tries to use high index diffraction planes to improve resolving power. Therefore, EXAFS measurement at high-energy regions is practically impossible, because reflections from high index planes must be used in order to get the resolution required. The use of a SSD (solid-state detector) to pick out the x rays from proper reflection partially resolved this problem,[9] and spectra at higher-energy regions up to 25 keV have been reported.[18,19] But I_0 and I must be measured alternatively in this case, making the quality of the data subject to fluctuations of the x-ray source during the measurement time of I_0 and I. In addition, when higher order is used, filters are necessary to reduce strong lower-order reflections, resulting in a serious attenuation in intensity. A simple method to avoid these problems is to use crystal planes such as Ge(553),[12] whose index is high enough to warrant resolution but has no low-order reflection. High index planes, however, have low reflectivity, and reflections which should not appear from structure factors often deteriorate the spectra because of the imperfection of crystals.

In this article a spectrometer which eliminates the above-mentioned problems by the use of two bent crystals is described. Resolution is mainly determined by the first monochromator, and the second monochromator serves to filter out the reflections of unnecessary order. Consequently, monochromatic as well as intense x rays are available over a wide energy range by applying high accelerating voltage to the x-ray tube. As a result, a spectrum with sufficient signal-to-noise ratio for EXAFS analysis can be obtained by a si-

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multaneous detection of I_0 and I within a few hours. With this spectrometer the spectral range covered is from 7 to 26 keV, within which the K absorption edge from Fe to Ag is included. Typically 200 000 counts/s can be obtained with resolving power better than 1000.

I. SYSTEM CONFIGURATION

A schematic configuration of the two-crystal EXAFS spectrometer is shown in Fig. 1. A Johansson-type ground and bent crystal monochromatizes the x-ray beam emanating from the source and focuses it onto the intermediate slit. Then the x rays diffracted by various index planes are again diffracted by the second Johansson-type crystal in the plus position and focused to the exit slit. A combination of crystals with different extinction rule for reflection yields a high intensity monochromatic beam without contamination of unnecessary diffraction. The incident beam flux I_0 and the transmitted photon I are measured simultaneously to compensate the source fluctuation. A semitransmitting ionization chamber just behind the exit slit monitors I_0. Either another ionization chamber, a scintillation counter, or SSD is placed to detect I, with room for the sample between the detectors.

A. X-ray source

The x rays are generated by a rotating anode x-ray generator, Rigaku RU-200 (60 kV, 200 mA). By the use of the line focus anode and at a take-off angle of 6°, the size of the x-ray source is 10×0.05 mm^2. Since the brehmsstrahlung flux emanating from the source depends on the atomic number of the target material as well as the accelerating voltage and the tube current, a material with high atomic number is preferred. Therefore, Au or Ag anodes are employed. In passing, these are found to be more resistant to the deposition of tungsten from the filament than Mo anodes.

Strong characteristic lines from tungsten often distort the spectra due to counting loss or nonlinearity of the detector. In order to eliminate this, the generator was modified in such a way that the tube current can be controlled through an analog interface of a computer. If I_0 changes more than a preset value, the tube current is varied to keep the intensity constant, typically within 5%.

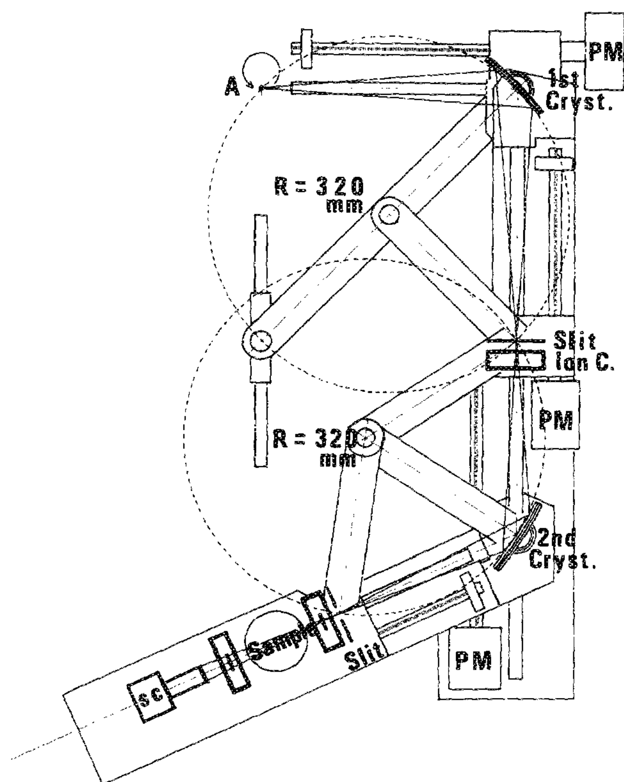

FIG. 1. A schematic diagram of the double-crystal EXAFS monochromator. A: rotating anode; I: ionization chamber; Ion C: ionization chamber for the alignment of the first monochromator; SC: scintillation counter or solid-state detector; PM: pulse motor. Dots represent two Rowland circles.

B. Monochromator

The principle for the first monochromator is the same as already reported.[9] In short, the x-ray source, a Johansson cut crystal, and the slit are maintained on a Rowland circle by two bars and two translational stages. The crystal of the second monochromator is placed on a stage which mounts the slit of the first monochromator (intermediate slit) and moves freely, floating above the base by an air bearing. The intermediate slit, the second crystal, and the exit slit are mounted on three arms of equal length which are held together with one common pivot (the center of the second Rowland circle). The crystal is fixed on an arm and the surface normal is directed to the center. The distance between the intermediate slit and the crystal is kept to be the same as the distance between the crystal and the exit slit by two translation stages during scanning, so as to fulfill the Bragg condition. An accurate as well as smooth translational motion without backlash was attained by a combination of a circulating linear ball bearing and a five-phase stepping motor. With the aid of arms and leads which restrict the movements of the crystals and slits, the motions required to scan are just two translations for each monochromator, making alignment and control very simple and reliable.

Because the efficiency and resolution of a curved crystal monochromator depend in opposite ways on the focusing circle, any value of Rowland radius R is a compromise of the two. Rowland radii of 300–350 mm have been most frequently employed in the literatures,[4,7–9] and here, too, R of 320 mm was chosen for both monochromators. The crystal size is 25×50 mm^2. The wavelength λ is determined by the following equation

$$n\lambda = 2d\sin\theta = rd/R\,,$$

where θ is the angle of incidence, r is the distance between the x-ray source and the crystal which is kept equal to that between the crystal and the slit, d is the lattice parameter, and n is the order of reflection. Incident angle can be varied from 15° to 45° for the first monochromator, and from 9° to 25° for the second one. Efficiency of the second monochromator is typically 5%–10%.

The resolution of the monochromator obtained, as ex-

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pressed by the FWHM of several characteristic lines with slit width of 100 μ, is as follows; 6 eV with Ge(220) at 8.048 keV (measured with Cu$K_{\alpha1}$), 15 eV with Ge(440) at 17.479 keV (Mo$K_{\alpha1}$), and 18 eV with Ge(660) or with Ge(444) at 22.163 keV (Ag$K_{\alpha1}$).

C. Detector

Since x rays from the double-crystal monochromator are completely free from diffractions from other index planes, the energy resolution is not required for detectors. Then, an ionization chamber is the best choice for both the I_0 and I detector because of its simplicity, large dynamical range, and low cost. Ar gas is used in the low-energy region, while Xe gas is used in the high-energy region. Gas pressure ranges from 500 to 760 Torr and the chambers are operated at 200–400 V. The current from the ionization chamber, which is typically of the order of 10^{-12} A, is detected by a Keithley 616 electrometer. The output is converted to the frequency and then sent to a scaler which is connected with a microcomputer through a CAMAC bus.[9]

Either a NaI scintillation counter or a solid-state detector (SSD) can also be placed instead of the second ionization chamber and can be used as an I detector as long as the transmitted x rays are not intense enough to cause a counting loss. It is often very helpful to monitor the quality of the x-ray beam by the SSD and to make sure that no higher-order reflection is contaminated or no stray light impinges the detector. If either happens it leads to an apparent reduction in the absorbance and possibly gives a spurious structure in the spectra.

D. Crystals and throughputs

The crystal for the first monochromator must have high resolving power and adequate brightness, while good resolution is not necessary but high reflectivity is required for the second one. The various factors affecting the resolution and brightness of the curved crystal have been discussed in detail by Knapp *et al.*[2,5] The resolution mainly depends on two properties of the crystal; lattice parameter and penetration depth. Better resolution is achieved by using a high index plane, but high index planes have relatively low reflectivity. A deterioration in resolution occurs to LiF and Si at high energy, typically >10 keV, because of large penetration depth due to low absorption coefficient.

With the above considerations in mind, various combinations of the crystals have been tested among Ge(111), Ge(220), Ge(311), Ge(400), Si(111), LiF(200), and LiF(220). A combination of crystals having different structure factors such as Ge(220)–Ge(111) is preferable; the first harmonics from Ge(111) is absent because of the extinction rule and the next allowed reflection, from Ge(660)–Ge(333), is very weak. For example, when the x-ray generator was operated at as high as 55 kV and the energy of the monochromator having Ge(220) and Ge(111) crystals was set to be 8 keV, the count rate was 9300 counts/s for the first order and 560 counts/s for the third and higher order, although x rays with 24, 32, and 40 keV are allowed. At lower operating voltages higher-order reflections are virtually eliminated. The generator current was 10 mA and the widths of the intermediate and the exit slits were 0.2 and 5 mm in this measurement.

TABLE I. Various combinations of crystals and the energy range covered.

1st crystal	2nd crystal	Energy range covered
Ge(220)	Ge(111)	4.5–12.0 keV
Si(333)	LiF(200)	8.4–19.7 keV
Ge(440)	LiF(200)	8.8–19.7 keV
Ge(440)	LiF(220)	10.3–23.9 keV
Ge(444)	LiF(220)	10.8–27.8 keV
Ge(800)	LiF(220)	12.4–27.8 keV
Ge(660)	LiF(220)	13.2–27.8 keV

The best combinations at several energies are given in Table I and the photon numbers obtained are represented in Fig. 2 as a function of applied voltage. Ge crystals are almost always chosen as the first monochromator crystal because of their resolution and high reflectivity. The fluorescence from Ge, which often makes a noise source, is completely sup-

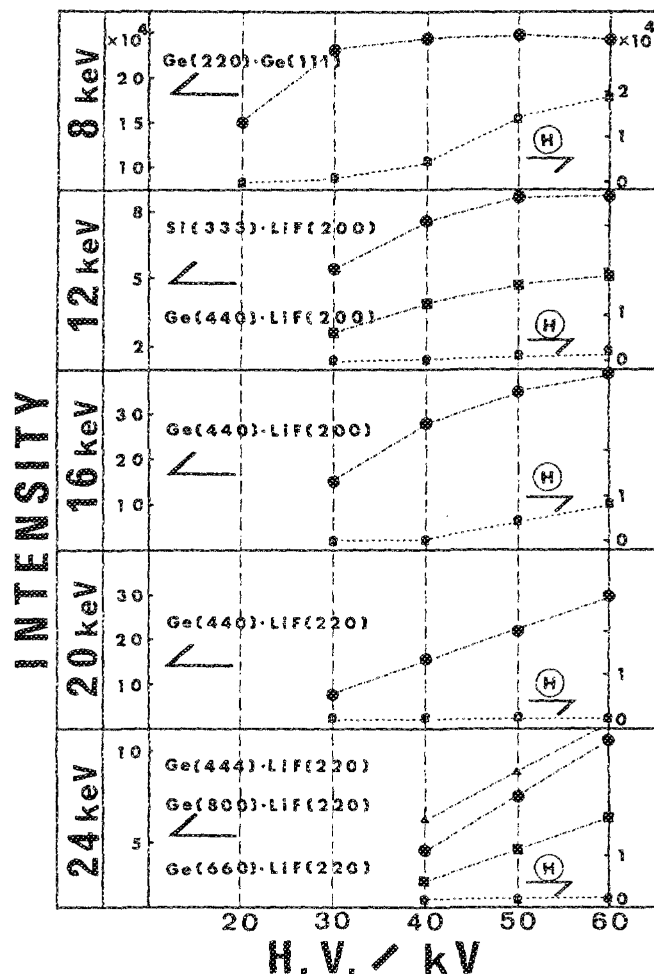

FIG. 2. Photon numbers in counts/s obtained by the use of various combinations of crystals at several energies as a function of the source voltages. Current is kept to be 200 mA. Open circles connected by dashed lines indicate the total photon number of the higher-order reflections and correspond to the numbers in the right.

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pressed by the second monochromator. Ge crystals are not adequate around 11 keV because of their characteristic absorption edge. Instead, Si crystal should be used in the 11–13 keV energy range. The first choice of the crystals around 16 keV was Ge(440)–Ge(311). Because of the low reflectivity of Ge(311) crystal, however, Ge(440)–LiF(200) gave better throughput with much less harmonics than anticipated. As is noticed from Fig. 2 the intensity of low-energy x rays shows saturation with applied voltages. For instance, the intensity of x ray at 8 keV does not increase very much over 35 keV, while that of higher harmonics increases almost linearly. Therefore, it is necessary to operate the x-ray generator below the saturation voltage at low energies.

II. PERFORMANCES

To test the performance of the present system we measured and analyzed the EXAFS spectra of several compounds which have absorption edges in high-energy regions. Shown in Fig. 3 are the EXAFS spectrum of Rh metal (absorption edge ~23.2 keV), the extracted oscillation, and the associated Fourier transforms. This spectrum was obtained with the combination of Ge(444)–LiF(220) in 10 h, collecting at least 5×10^6 photons as I at each data point. The Fourier transform exhibits features characteristic of fcc metals, proving the quality of data obtained with this system. A small peak at 1.8 A is not due to noise, but is a consequence of the complex nature of the amplitude and phase-shift functions of high atomic number elements and is always observed in the literature.[19]

To assess the quality of data about catalytically interesting materials, EXAFS of a commercially available hydrodesulfurization catalyst Co–Mo/γ–Al_2O_3 (Mo content 10 wt. %) was studied in a sulfided form. Mo EXAFS (absorption edge ~20 keV) taken with the combination of Ge(440)–LiF(220) is shown in Fig. 4 as well as the associated Fourier transform. Two peaks due to Mo–S and Mo–Mo in the transform, which resembles, but is not the same as that of MoS_2, offer interesting information about the local structure of Mo in this catalyst.

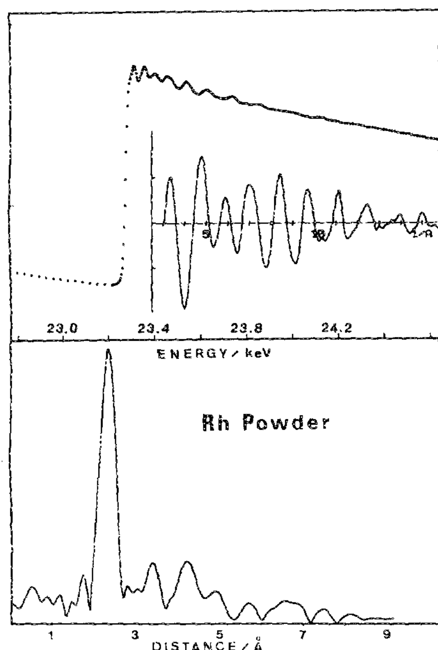

FIG. 3. An EXAFS spectrum of Rh metal powder taken at RT. Ge(444)–LiF(220) was used with slit width of 100 μ. The extracted oscillation and the associated Fourier transform are also shown.

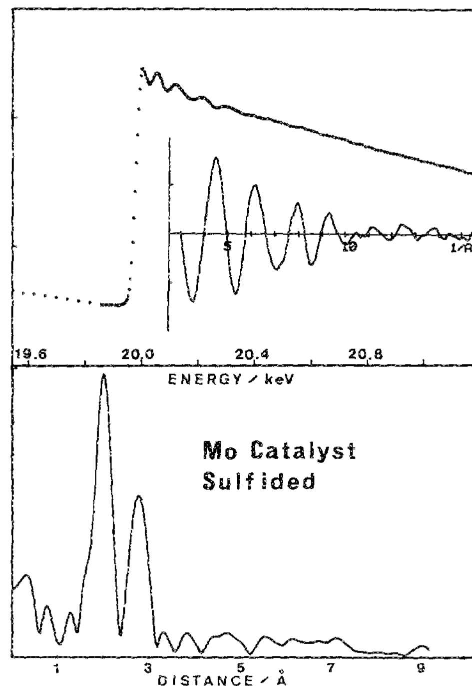

FIG. 4. An EXAFS spectrum of a commercial Mo catalyst in a sulfided form. Ge(440)–LiF(220) was used with slit width of 100 μ. The extracted oscillation and the associated Fourier transform are also shown.

In conclusion, the present system can supply accurate EXAFS spectra over a wide energy range with a conventional x-ray source. It is especially useful in the high-energy region where the second row transition metals have absorption edges, and opens up wide possibilities of EXAFS studies of various substances in laboratory scale.

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[1] P. A. Lee, P. H. Citrin, P. Eisenberger, and B. M. Kincaid, Rev. Mod. Phys. **53**, 769 (1981).
[2] *American Institute of Physics Conference Proceedings*, Vol. 64, edited by E. A. Stern (American Institute of Physics, New York, 1981).
[3] G. S. Knapp, H. Chen, and T. E. Klippert, Rev. Sci. Instrum. **49**, 1658 (1978).
[4] G. G. Cohen, D. A. Fischer, J. Colbert, and N. J. Schevchik, Rev. Sci. Instrum. **51**, 273 (1980).
[5] P. Georgopoulos and G. S. Knapp, Appl. Crystall. **14**, 3 (1981).
[6] S. Khalid, R. Emrich, R. Dujari, J. Schultz, and J. R. Katzer, Rev. Sci. Instrum. **53**, 22 (1982).
[7] A. Williams, Rev. Sci. Instrum. **54**, 193 (1983).
[8] W. Thulke, R. Haensel, and P. Rabe, Rev. Sci. Instrum. **54**, 277 (1983).

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[9]K. Tohji, Y. Udagawa, T. Kawasaki, and K. Masuda, Rev. Sci. Instrum. **54**, 1482 (1983).
[10]F. W. H. Kampers, F. B. M. Duivenvoorden, J. B. A. D. Van Zon, P. Brickgreve, M. P. A. Viegers, and D. C. Koningsberger, Solid State Ionics **16**, 55 (1985).
[11]M. Sano, T. Maruo, and H. Yamatera, Bull. Chem. Soc. Jpn. **57**, 2757 (1984).
[12]Y. Yacoby, M. Brettschneider, and M. Bezalel, Rev. Sci. Instrum. **58**, 588 (1987).
[13]U. Kaminaga, T. Matsushita, and K. Kohra, Jpn. J. Appl. Phys. **20**, L355 (1981).
[14]K. Taniguchi, N. Yamaki, and S. Ikeda, Jpn. J. Appl. Phys. **23**, 909 (1984).
[15]K. Tohji, Y. Udagawa, S. Tanabe, T. Ida, and A. Ueno, J. Am. Chem. Soc. **106**, 5172 (1984).
[16]K. Tohji, Y. Udagawa, T. Mizushima, and A. Ueno, J. Phys. Chem. **89**, 5671 (1985).
[17]K. Tohji, Y. Udagawa, M. Harada, and A. Ueno, J. Chem. Soc. Jpn. 1553 (1986).
[18]Y. Udagawa, K. Tohji, Z. Z. Lin, T. Okuhara, and M. Misonou, J. Phys. **47**, C8-249 (1987).
[19]G. Meitzner, G. H. Via, F. W. Lytle, and J. H. Sinfelt, J. Chem. Phys. **78**, 2533 (1983).

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