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EXAFS Spectroscopy of Some Iron(III) Compounds by Use of Dispersive-type In-laboratory X-Ray Spectrometer

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A dispersive-type in-laboratory EXAFS spectrometer was constructed by combining a transmission-type dispersing crystal and a position-sensitive proportional counter. FeK absorption spectra were measured by use of this apparatus on $FeCl_3 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$ and anhydrous $FeCl_3$. Discussion is given on the results obtained from the analyses of observed EXAFS data concerning the structure around Fe ions in these compounds. AsI_3-like structure is proposed for anhydrous $FeCl_3$.

Extended X-ray absorption fine structure (EXAFS) spectroscopy has rapidly grown up to the most important method to study the local structure around an X-ray absorbing atom in solids and liquids since its usefulness as a structural tool was first demonstrated by Stern *et al.*[1–5)]

This rapid development of EXAFS spectroscopy also comes from the utilization of synchrotron radiation. Because usually EXAFS oscillation is only a few percent or less of absorption coefficient, we need to measured absorption coefficient of a sample with a high accuracy as a function of X-ray wavelength over the concerned spectral region. It takes a very long measuring time to obtain reliable EXAFS data if we use a conventional X-ray spectrometer composed of an ordinary X-ray source and a crystal monochromator. The time required to obtain EXAFS data has been drastically shortened by use of synchrotron radiation. This has opened wide new fields of application of EXAFS spectroscopy.

Although the use of synchrotron radiation is evidently of great value in EXAFS spectroscopy, the use of a synchrotron radiation facility inevitably has various restrictions concerned with place and time. For some type of applications, there are large advantages of having an in-laboratory EXAFS spectrometer if it can provide EXAFS data of satisfactory quality with a tolerable measuring time. Even if one is considering to use a synchrotron radiation facility to obtain accurate EXAFS data, it may be of great value to carry out preliminary experiments with an in-laboratory apparatus.

One approach to reduce the data acquisition time of an in-laboratory EXAFS spectrometer is naturally to increase X-ray intensity as high as possible by employing a very-high-power X-ray generator[6)] and/or a bent-crystal monochromator.[7,8)] In fact, it was reported by Cohen *et al.*[9)] that the time required to obtain EXAFS data could be markedly reduced by combining a bent-crystal monochromator with a high-power rotating anode X-ray generator.

Another approach is to improve the data collection efficiency by simultaneously measuring the intensities of X-rays over the concerned spectral region by use of a system composed of a dispersing crystal and a position-sensitive detector.[10,11)] We constructed an EXAFS spectrometer by use of transmission-type dispersing method which has been developed by Kaminaga *et al.*,[10)] and studied FeK EXAFS of $FeCl_3 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$, and anhydrous $FeCl_3$.

EXAFS Spectrometer

Figure 1 illustrates the principle of the EXAFS spectrometer constructed in the present study. When a divergent white X-ray beam hits the surface of a thin single crystal, X-ray incident direction is different at different positions of the crystal surface, hence the X-ray wavelength which satisfies the diffraction condition, is different at different positions. It may be easily understood from a geometrical consideration that X-rays of different wavelengths which have been diffracted at different positions, will be focused at the position (SP in Fig. 1) which is symmetrical to the X-ray source (X) with respect to the diffracting crystal, and then diverge. Thus the diffracting crystal works as a transmission type X-ray polychromator. With this optical system, X-ray intensities over the interested spectral region can be simultaneously measured by placing a position-sensitive detector at some distance after the focusing position. An absorption Spectrum can be obtained by performing intensity measurements with and without a sample in the X-ray path. Most conveniently a sample is placed at the focusing position, since the sample area in X-ray path, hence the required sample amount will be minimized and, at the same time, the troubles concerned with the ununiformity of the sample can be largely avoided.

We used a molybdenum sealed X-ray tube (Philips

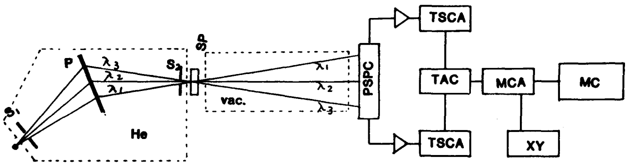

Fig. 1. Block diagram of EXAFS spectrometer.
S: Slit, P: dispersing crystal, SP: sample, PSPC: position sensitive proportional counter, TSCA: timing single channel analyzer, TAC: time to amplitude converter, MCA: multi-channel analyzer, XY: X-Y recorder, MC: micro-computer system.

fine focus tube or Toshiba normal focus tube) as the X-ray source, which was operated with a conventional X-ray power supply (Rigaku D-2F, 1 kW) mostly with 25 mA at 20 kVp. A silicon single crystal of 50 μm thick was used as the dispersing crystal, Si(111) plane having been chosen as the diffraction plane so that the (222) harmonics could be eliminated. Both the distance from X-ray source to silicon crystal and that from the crystal to sample were 250 mm, and the distance from sample to detector was mostly set as 600 mm. In order to minimize X-ray intensity loss, the X-ray path between source and sample was replaced with helium gas, and that between sample and detector was evacuated with a mechanical vacuum pump. By this way, available X-ray flux became 2.5 times of that obtainable when all X-ray path is in the ordinary atmosphere.

We used a multi-cathode position-sensitive proportional counter (PSPC) of delay line readout type as the detector. For the gas filled in PSPC, we used either PR gas (Ar 90%, $CH_3$10%) or Xe-CH_4 mixture (Xe 90%, CH_4 10%), pressurized to about 3 kg cm^{-2}. The block diagram of the electronic system is also shown in Fig. 1. The information about the incident position of an X-ray photon is taken out as the signal pulse height, which is digitized through an ADC (NAIG E-551) to determine the address in a process memory (NAIG E-562) at which the count is to be stored. After count data have been sufficiently accumulated, the data are transfered to a microcomputer (NEC PC-8001), with which initial data treatments are carried out.

By examining the X-ray spectrum recorded on a photographic film placed at the position of the detector, the spectral resolution of our optical system was confirmed to be about 4 eV around the FeK absorption edge, but the overall resolution of obtained EXAFS data was about 7 eV or a little more, because of the positional resolution of our detection system. Although we used a conventional sealed X-ray tube operated at a low power, we were able to obtain EXAFS data within a torelable measuring time. For example, the FeK absorption spectrum (shown in Fig. 2) of an iron foil of 4 μm thick was obtained with a measuring time of about 4 h with a fine-focus Mo X-ray tube operated with 25 mA at 20 kVp, taking 10^5 counts at each measured energy point, the number of measured points being 250 over the observed spectral region, 6.7—8.3 keV.

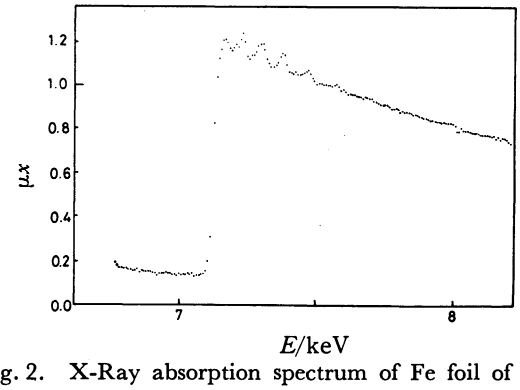

Fig. 2. X-Ray absorption spectrum of Fe foil of 4 μm thick. The data acquisition time was 3 h 45 min.

EXAFS of Some Fe(III) Compounds

By use of the apparatus described in the preceeding section, we obtained EXAFS data on $FeCl_3 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$, and anhydrous $FeCl_3$. In the cases of $FeCl_3 \cdot 6H_2O$ and $Fe(ClO_4)_3 \cdot 6H_2O$, crystalline powder was mixed with well-dried Nujol to be used as the sample for EXAFS measurement, and FeK absorption spectra were measured by keeping such a mixture between two polyethylene plates separated with a PTFE spacer of an appropriate thickness. A special care had to be taken for the deliquescence in the case of anhydrous $FeCl_3$. We prepared anhydrous $FeCl_3$ powder in a glove box filled with dry nitrogen, and carried out X-ray absorption measurement on a compaction of the powder kept in a dry nitrogen atmosphere. The measurement of FeK absorption spectrum was repeated two or three times on each sample to check the reproducibility.

Figure 3 shows the FeK absorption spectra of the three compounds. Note that the first peak near FeK absorption edge is very weak in the case of anhydrous $FeCl_3$ as compared with $FeCl_3 \cdot 6H_2O$ and $Fe(ClO_4)_3 \cdot 6H_2O$. This difference is likely to be associated with the difference in the number of the H_2O molecules coordinated around Fe ion. Another aspect that can be seen clearly from the comparison of the three spectra, is the difference of the position of third peak.

We extracted EXAFS oscillations from the observed spectra and analyzed them to derive structural information. The analysis was performed by use of the computer program system written by Sato in our laboratory.[12] The program system consists of the programs for background subtraction, extraction of EXAFS oscillation $\chi(k)$, Fourier transformation of $k^n\chi(k)$, Fourier filtering and back transofrmation, and curve-fitting analysis. In the curve-fitting analysis, we assumed the following formula for $\chi(k)$.

$$\chi(k) = C_0 \sum_i N_i k^{-1} r_j^{-2} F_i(k) \times \exp(-2\sigma_i^2 k^2) \cdot \sin[2kr_i + \phi_i(k)] \qquad (1)$$

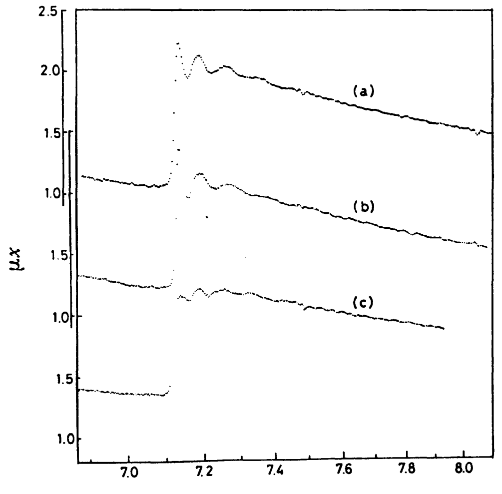

Fig. 3. X-Ray absorption spectra of (a) $FeCl_3$–$6H_2O$, (b) $Fe(ClO_4)_3$–$6H_2O$, and (c) Anhydrous $FeCl_3$.

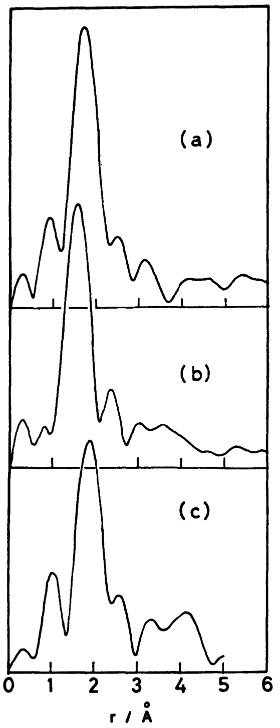

Fig. 4. Fourier transforms of $k^3\chi(k)$ for (a) $FeCl_3 \cdot 6H_2O$, (b) $Fe(ClO_4)_3 \cdot 6H_2O$, and (c) anhydrous $FeCl_3$.

where N_i and r_i are the number and distance of atom(i), $F_i(k)$ and $\phi_i(k)$ are back-scattering amplitude and phase shift, σ_i is Debye-Waller factor, and C_0 is a normalizing constant. In the present study, we used theoretical $F_i(k)$[13] and $\phi_i(k)$,[14] and treated C_0, r_0, and σ_i as adjustable parameters, an appropriate assumption being done on N^i value. We introduced the following R index as the measure of the agreement between experimental and calculated $k^n\chi(k)$.

$$R(k^n\chi) = \sqrt{\frac{\sum_j [k^n\chi_{\mathrm{exptl}}(\chi_j) - k^n\chi_{\mathrm{calcd}}(k_j)]^2}{\sum_j [k^n\chi_{\mathrm{exptl}}(k_j)^2]}}$$

All calculations were performed by use of a HITAC M-200H at the Computer Center of The University of Tokyo.

The results of Fourier transformation of $k^3\chi(k)$ are shown in Fig. 4. A prominent peak is found around 2 Å for all three compounds studied here. This peak corresponds to the first back-scattering shell around Fe ion, its position being a little different for the three salts reflecting the difference of the local structure around Fe ion. Fe ion is likely to be surrounded by six oxygen atoms of coordinating H_2O molecules in $Fe(ClO_4)_3 \cdot 6H_2O$, while it is surrounded by six chlorine ions in anhydrous $FeCl_3$. In $FeCl_3 \cdot 6H_2O$, Fe ion is known to be surrounded by two chlorine ions and four oxygen atoms of coordinating H_2O molecules.[15] Thus it seems quite reasonable that the peak due to the first back-scattering shell is shift to larger distance in anhydrous $FeCl_3$ in comparison with other two compounds.

Back-Fourier transforming the region of the above-mentioned peak, we carried out curve-fitting analysis. The results are summarized in Table 1, the experimental and calculated $k^3\chi(k)$ curves being shown in Figs. 5

Table 1. Bond distances obtained by the analyses of EXAFS data of Fe(III) compounds

The coordination numbers assumed in the analyses are given in parentheses.

Sample		Bond	Bond length d/Å	
			(EXAFS	diffraction)
$FeCl_3 \cdot 6H_2O$		Fe–Cl(2)	2.28	$2.30^{\text{a)}}$
		Fe–O(4)	2.03	$2.07^{\text{a)}}$
$Fe(ClO_4)_3 \cdot 6H_2O$		Fe–O(6)	2.00	—
$(Fe(NO_3)_3 \cdot 9H_2O$		Fe–O	—	$1.99^{\text{b)}}$
$FeCl_3$	(Model 1)$^{\text{d)}}$	Fe–Cl(6)	2.25	$2.48^{\text{c)}}$
	(Model 2)$^{\text{e)}}$	Fe–Cl(3)	2.24	
		Fe–Cl(3)	2.59	

a) From Ref. 15. b) Average of six Fe–O bond lengths, from Ref. 16. c) From Ref. 17b. d) Octahedrally coordinated model (BiI_3-like structure). e) AsI_3-like structure.

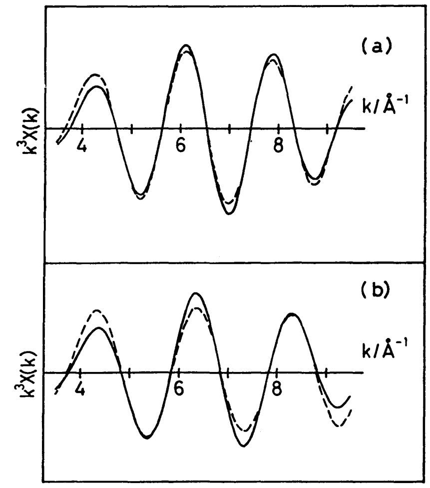

Fig. 5. Curve-fitting results of (a) $FeCl_3 \cdot 6H_2O$ and (b) $Fe(ClO_4)_3 \cdot 6H_2O$ (——: experimental, ------: theoretical).

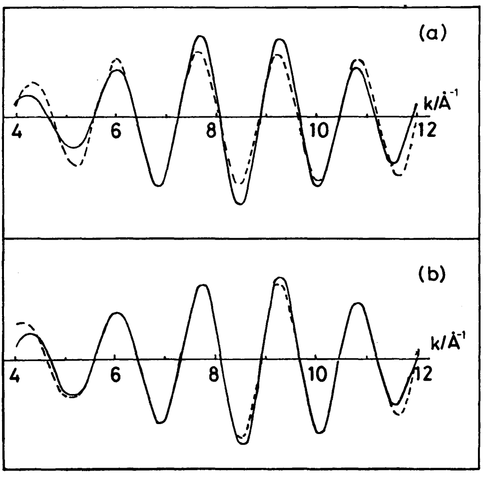

Fig. 6. Curve-fitting results of anhydrous $FeCl_3$: (a) one-shell fitting and (b) two-shell fitting (——: experimental, ------: theoretical).

and 6.

The crystal structure is known for $FeCl_3 \cdot 6H_2O$, according to which Fe ion is surrounded by two chlorine ions with the Fe–Cl distance of 2.30±0.02 Å and four oxygen atoms of H_2O with the Fe–O distance of 2.07±0.02 Å.[15] We performed curve-fitting analysis assuming two back-scattering shells, the one corresponding to four oxygen atoms and the other corresponding two chlorine ions. The best-fit result gave 2.03±0.02 Å for Fe–O and 2.28±0.04 Å for Fe–Cl. These values are in good agreement with the distances known from the crystal structure analysis. This indicates the reliability of our EXAFS data and that of the analysis.

In the case of $Fe(ClO_4)_3 \cdot 6H_2O$, the crystal structure is not known, but there is a good reason to believe that six H_2O molecules are coordinating to Fe ion as in the crystal of $[Fe(H_2O)_6](NO_3)_3 \cdot 3H_2O$.[16] Our EXAFS data are consistent with this assumption. The curve-fitting analysis gave 2.00±0.02 Å for Fe–O distance, which coincides well with 1.986±0.017 Å found by the crystal structure analysis of $[Fe(H_2O)_6] \cdot (NO_3)_3 \cdot 3H_2O$ for the average Fe–O distance between Fe ion and octahedrally coordinating H_2O molecules.[16]

Anhydrous $FeCl_3$ has been considered to have bismuth iodide structure, namely an iron ion is assumed to be surrounded by six chlorine ions with equivalent Fe–Cl distance.[17] Using this model, Fe–Cl distance in anhydrous $FeCl_3$ was deduced to be 2.48 Å from the observed lattice parameters.[17b] From the curve-fitting analysis of EXAFS data, we obtained 2.25±0.05 Å for Fe–Cl distance under the assumption that Fe ion is surrounded by six equivalent chlorine ions. This value is 0.23 Å shorter than the interatomic distance estimated from the lattice parameters. The discrepancy between the two values seems to be too large to be ignored when we consider the fact that the interatomic distances determined from EXAFS data coincide well with those from diffraction data in the cases of other two compounds. If Fe ion is actually surrounded by six equivalent chlorine ions with the Fe–Cl distance of 2.25 Å, the spacing between the two chlorine layers which are sandwiching Fe ions will be 1.98 Å and that between the other pair of chlorine layers will be 3.84 Å. The former value seems to be too small while the latter seems to be too large in comparison with the ionic radius of chlorine ion.

It is worthwhile to note that, although AsI_3 and SbI_3 were previously believed to have bismuth iodide structure,[17a] the detailed crystal structure analyses revealed latter that these compounds were built up from discrete triiodide molecules such as AsI_3 (or SbI_3), consequently six iodine atoms surrounding As (or Sb) atom are not at equivalent distance, three being at a shorter distance and three others at a longer distance.[18,19] Thus we analyzed the EXAFS data of anhydrous $FeCl_3$ with two-shell model assuming AsI_3-like structure. The curve-fitting analysis gave 2.24±0.05 Å and 2.59±0.05 Å for the two Fe–Cl distances with an excellent agreement between the experimental and calculated $k^3\chi(k)$ (Fig. 6b); the R index was found to be only 0.155 while it was 0.274 in the analysis with one-shell model (Fig. 6a). Therefore it is most likely that anhydrous $FeCl_3$ has AsI_3-like structure.

Summary

We constructed an in-laboratory EXAF Sspectometer combining a transmission-type dispersing crystal with a position-sensitive proportional counter, and demonstrated that EXAFS data of a sufficient quality for structural study could be obtained with a torelable measuring time. This EXAFS spectrometer is easily constructed with a relatively small cost, and might have wide applications.

By analyzing EXAFS data obtained on $FeCl_3 \cdot 6H_2O$, $Fe(ClO_4)_3 \cdot 6H_2O$ and anhydrous $FeCl_3$ by use of the constructed in-laboratory apparatus, we studied the local structures around Fe ions, and showed that anhydrous $FeCl_3$ has AsI_3-like structure, having three chlorine atoms at a shorter Fe–Cl distance and other three chlorine atoms at a longer Fe–Cl distance.

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