October, 1984] © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 2757—2760 (1984) 2757

Development of a Laboratory EXAFS System and Its Application to Aqueous Nickel(II) Ammine Solutions

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(Recieved May 1, 1984)

A laboratory EXAFS system with a curved crystal has been developed. This apparatus consists of a usual X-ray tube, a spectrometer with a Johan-type curved crystal, and two proportional counters detecting the X-rays. The resolution and performance tests have been carried out and excellent spectra have been obtained for NiO. With this system, aqueous solutions of ammine and ethylenediamine nickel(II) salts have been studied. The spectra were analyzed by the curve-fitting method by reference to the spectra of appropriate crystals containing the corresponding complexes. The values obtained for the Ni–N distances are 2.12±0.01 Å. These values are very close to those of the corresponding complexes in crystals.

The extended X-ray absorption fine structure (EXAFS) technique for the study of the molecular structure has made a rapid development and has been applied to a variety of problems.[1] Synchrotron orbital radiation (SOR) is evidently of great value in EXAFS spectroscopy; however, the use of an SOR facility is inevitably accompanied by various restrictions as to place and time.

In previous papers, we reported EXAFS studies of aqueous cyanocuprate(I)[2] and copper(II) ammine[3] solutions with a laboratory system equipped with a position-sensitive photodiode array. The system has advantages of high efficiency in the data collection and of little dependence on the X-ray flux fluctuation with time. This detector has an excellent position resolution (28μ/channel) which may be applied for SOR facilities[4] and for a small angle scattering apparatus[5] as a highly efficient X-ray detector. However, continuous X-rays generated by the tube contain many characteristic lines from the target as well as contaminants. When the photodiodes detect all the X-rays without energy resolution, the voltage applied to the anode of the X-ray tube is restricted in order to avoid the contamination of the higher-order reflections; then the brightness of the continuous X-rays is kept at low. Thus the application of our system with a photodiode array is limited to particular kinds of chemical elements.

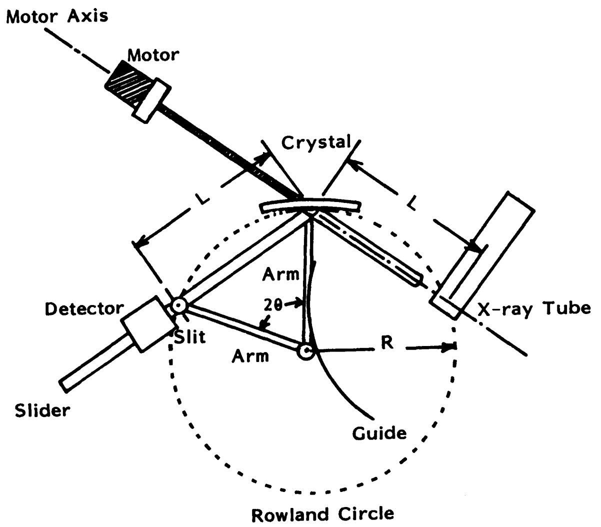

Fig. 1. Schematic diagram of the X-ray monochromator with a Johan-type curved crystal.

In order to extend the EXAFS study of solution systems, we have developed a new laboratory EXAFS system with a Johan-type curved crystal. We have carried out its performance test and then applied the method to the structural study of aqueous solutions of ammine and ethylenediamine nickel(II) salts.

Ammine complexes of metal ions are the most fundamental and important species in coordination chemistry. Fujita and Ohtaki[6] studied the structure of the aqueous ethylenediamine nickel(II) solutions by the X-ray diffraction technique. They reported Ni–N distances of 2.10 Å for the bis-complex and 2.20 Å for the tris-complex. X-ray studies of the solid tris-ethylenediamine complex salts[7–10] gave about 2.1 Å for the Ni–N bond distances; the results on solutions are not consistent with those on crystals. Our EXAFS results will be given below.

System Configuration

The laboratory EXAFS system consists of three parts; a usual X-ray generator, a spectrometer with a curved crystal, and an X-ray detector system. The X-ray spectrometers with a bent crystal have been reported by Knapp *et al.*,[11] Williams,[12] Thulke *et al.*,[13] and Tohji *et al.*[14] The present system is basically of the same configuration as theirs, but has two features, the spectrometer with a Johan crystal and one stepping motor and the counter system with energy resolution activity.

A. X-ray Source. The X-rays are generated by a Rigaku 2kW X-ray generator equipped with a Philips fine focus X-ray tube with a Mo anode. The X-rays are emitted from a vertical square (8-mm high) on the anode. Its effective width at a take-off angle of 6° is about 0.04 mm.

B. Spectrometer. The basic geometrical arrangement for the EXAFS spectrometer is schematically shown in Fig. 1. The essential features of this instrument are the same as the Applied Research Laboratories design.[15] The anode of the X-ray generator, the LiF crystal ($2d$=4.027 Å) and the receiving slit are held on a Rowland circle. The guide, arms, and wires (not shown in Fig. 1) were provided to effect the following movements as a function of θ:

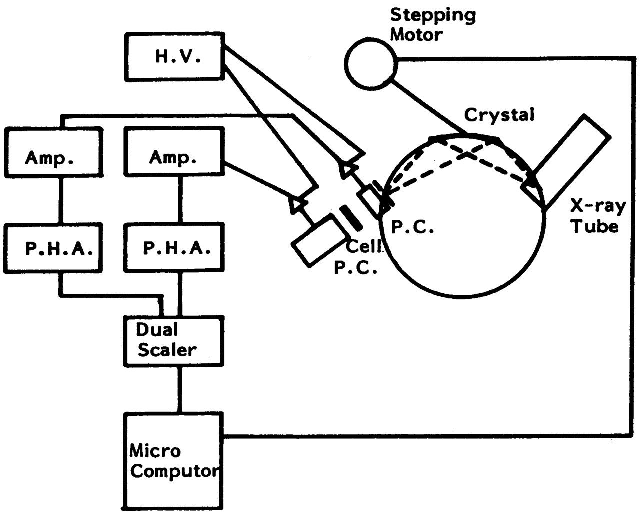

Fig. 2. Schematic diagram of the laboratory EXAFS system.

(1) The crystal moves on the motor-axis in a straight line away from the source aperture, thereby increasing the crystal-source distance, L, in accordance with $L=2R\sin\theta$. (2) The detector moves keeping the relation $r=2R\sin2\theta$, where r is the distance between the source and the detector. (3) The detector slit is always directed toward the center of the crystal. Above conditions have been accomplished by one stepping motor. As the Rowland geometry is satisfied, the radiation with $n\lambda=2d\sin\theta$ is Bragg-diffracted from the LiF crystal and subsequently focused at the receiving slit on the Rowland circle. The focusing by the Johan crystal is less satisfactory than that by the crystal of the Johansson type. However, the monochromator can be more easily adjusted.

C. Detection System. The block diagram of the detection system is shown in Fig. 2. Monochromatized X-ray coming through the receiving slit passes first through a proportional counter which monitors the intensity of the radiation incident on the sample(I_0). The intensity of the X-ray which is transmitted by the sample is then measured by the second proportional counter. The photon received by each counter is converted to an electric pulse, which is amplified, pulse-hight-analyzed and counted. Both signals from the first and the second proportional counters are counted until the number of signals detected by the first (I_0) counter reaches the preset-number of the dual scaler. After reading-out, the spectrometer is set to the next Bragg angle, and both counters are started again. The spectra are stored on a magnetic disk of a microcomputer (SORD M223-Mark V) which also controls the stepping motor. A high voltage supply (1.6 kV) operates the two proportional counters (90% Ar–10% CH_4 gas flow at 1 atm).

Performance

The resolution of an X-ray spectrometer based on the Johan crystal optics is lower than that based on the Johansson's. The experimental resolution was obtained from the measured intensity profile of the characteristic emission lines of the impurity copper contained in the anode of the X-ray tube. Figure 3 shows the *Kα* doublet of Cu. A resolution satisfactory for measuring EXAFS was obtained when the receiving slit was set to 0.1 mm. In these conditions, the X-ray source operating at 16 kV and 5 mA gave an X-ray flux of 5×10^4 cps.

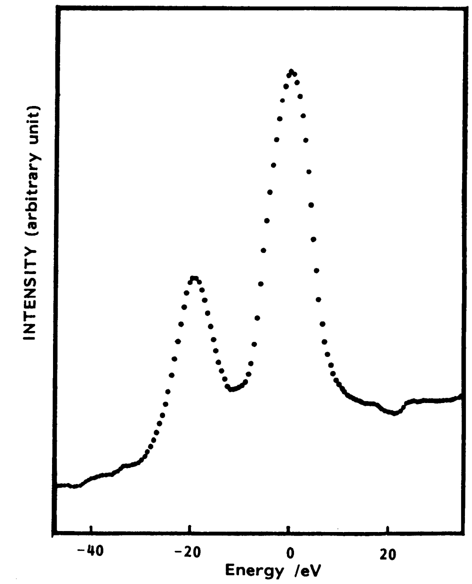

Fig. 3. Cu *Kα* doublet obtained with a LiF(220) Johan-type crystal.

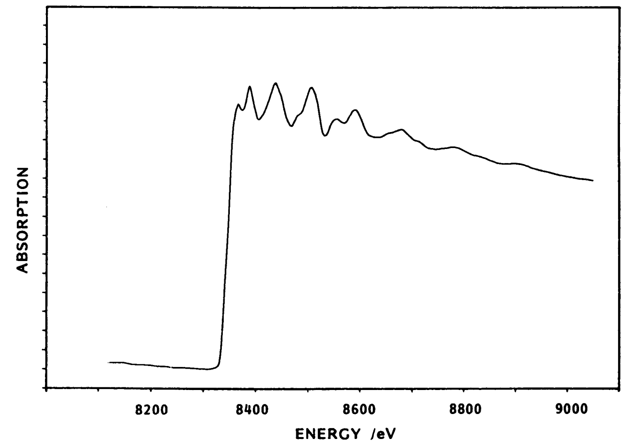

Fig. 4. X-ray absorption spectrum of 5-μm thick Ni foil.

Since metal foil shows a pronounced EXAFS and is easily available, it has widely been used as a standard sample in EXAFS measurements. Figure 4 shows the absorption spectrum of Ni foil obtained from a run of 4-h measurement at 16 kV and 5 mA. The feature is almost identical with that obtained with SOR.

As an example of the results obtained for substances of chemical interest, the subtracted EXAFS oscillation $\chi(k)$ and the Fourier transform of $k^3\chi(k)$ of NiO powder are shown in Fig. 5(a) and (b). EXAFS up to 14 Å^{-1} in the k range above the edge is clearly seen. The Fourier transform indicates the existence of some atoms, all in accordance with the known crystal structure when the phase shift is taken into account.

It is often quoted that characteristic lines from contaminated anode materials seriously impair the

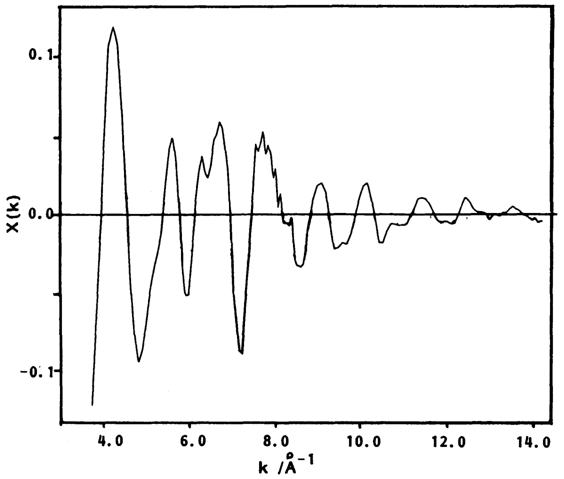

Fig. 5a. EXAFS spectrum of NiO.

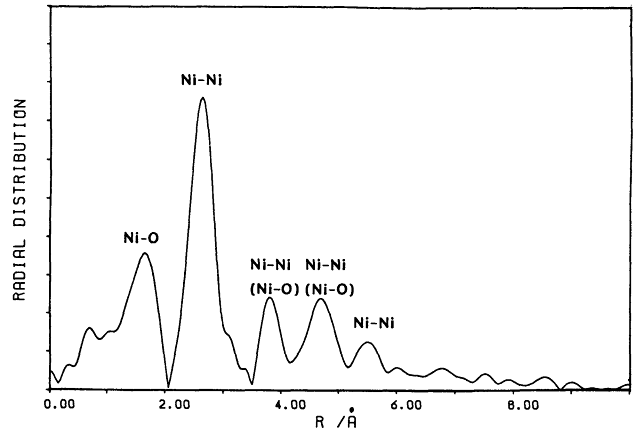

Fig. 5b. Fourier transformation of Fig. 5a.

quality of EXAFS spectra. For example, the L_α and L_η lines of W from the filament overlap the absoption spectrum of Ni. However, this difficulty can be avoided with a proper electronic circuits employed here. Measurements on two examples evidenced that the present system can give spectra good enough for a practical EXAFS analysis.

It is worth to discuss the advantage of the use of the proportional counter system over an ion-chamber system for the X-ray flux of our laboratory apparatus. The leak current of the ion chamber may be of the order of 10^{-16} A, which corresponds to *ca.* 10^3 photons. When the X-ray flux is high, for example 10^{10} photons/s, as in SOR, this leak current causes no trouble. But it is serious matter in a laboratory spectrometer operating with 10^6—10^5 photons/s. Although the photon counting systems with proportional (and scintillation) counters need the correction for the dead time in a higher X-ray flux, a proportional counter with a proper electronic circuit is preferred in this case.

Experimental

Aqueous solutions of ammine and ethylenediamine nickel(II) salts were prepared by dissolving $Ni(NO_3)_2 6H_2O$ in aqueous solutions of ammonia and ethylenediamine. The concentrations were determined by standard methods; Ni (0.300 M (1 M=1 mol dm^{-3})) and NH_3 (6.58 M) for ammine solution and Ni (0.292 M) and en (1.05 M) for ethylenediamine solution. The known stability constants show that the main species contained in these solutions are $[Ni(NH_3)_6]^{2+}$ for the ammine and $[Ni(en)_3]^{2+}$ for the ethylenediamine solutions. A plastic cell contained a small volume of the sample solution between windows spaced 1.0 mm apart. The solid sample was well grounded and deposited on to a piece of scotch-tape.

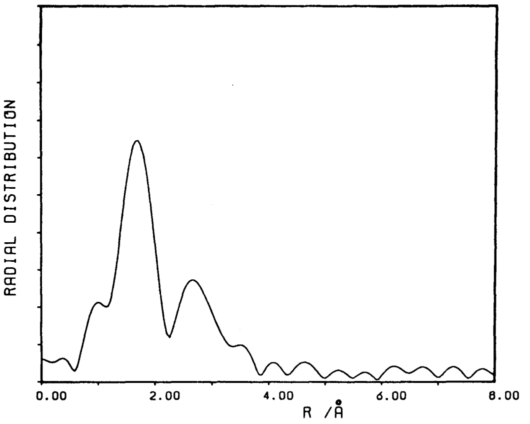

Fig. 6. Fourier transformation of the EXAFS spectrum of aqueous $[Ni(en)_3]^{2+}$ solution.

Data Analysis

The EXAFS spectra have been analyzed by following the standard procedure. The absorption background before the edge has been substracted from the experimental absorption spectrum, and the resulting spectrum $\mu(k)$ was normalized by using the atomic absorption coefficient $\mu_0(k)$, in order to give the χ(k) fine structure defined by $\chi(k)=[\mu(k)-\mu_0(k)]/\mu_0(k)$. The photoelectron wave vector is given by $k=[(E-E_0)2m/\hbar^2]^{1/2}$, where E is the photon energy and E_0, some reference energy which may not coincide with the energy of the absorption edge.

Result for the Solutions of the Ammine and Ethylenediamine Complexes

Figure 6 shows the results of Fourier transformation from the k space to the r space for aqueous $[Ni(en)_3]^{2+}$ solution. The radial distribution curve shows two peaks, of which the main one should correspond to the N atoms of the coordinated ethylenediamine ligands and the smaller one may be due to the C atoms of the ligands.

The curve-fitting analysis was performed according to the method of Cramer *et al.*[16] using the following formula.

$$k^2\chi(k) = c_0Nr^{-2}\exp(-c_1k^2)k^{-c_2}\sin[a_0+(a_1+2r)k+a_2k^2],$$

N and r represent the coordination number and the interatomic distance, respectively, and c_0—c_2 are the parameters for the amplitude functions and a_0—a_2 the phase shift parameters. To determine the parameter values, we first examined the spectra of the cryslalline $[Ni(en)_3]SO_4$ and $[Ni(en)_3](NO_3)_2$ of which the structures are known (r_{Ni-N}=2.124 Å for sulfate,[7] r_{Ni-N}=2.120 Å for nitrate,[8] and N=6 for both complexes).

TABLE 1. CROSS-CHECK OF THE RESULTS OF LEAST-SQUARES FITS TO EXAFS DATA FOR CRYSTALLINE $[Ni(en)_3](NO_3)_2$ AND $[Ni(en)_3]SO_4$

	Coordination number	Ni-N distance/Å
$[Ni(en)_3](NO_3)_2$	5.7±0.8(6.0)	2.11±0.01(2.120)[a]
$[Ni(en)_2]SO_4$	6.2±0.8(6.0)	2.13±0.01(2.124)[b]

a) Obtained with parameters derived from the EXAFS of $[Ni(en)_3]SO_4$. (The values in parentheses are the results of an X-ray diffraction study.[8]) b) Obtained with parameters derived from the EXAFS of $[Ni(en)_3](NO_3)_2$. (The values in parentheses are the results of an X-ray diffraction study.[7])

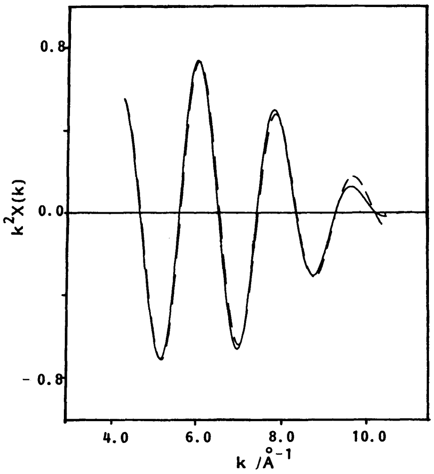

Fig. 7. First-shell fit for determining the structure of $[Ni(en)_3]^{2+}$ in solution by use of a set of parameters derived from the spectrum of solid $[Ni(en)_3]SO_4$. The solid line is the filtered EXAFS spectrum and dashed line is the least-squares fit.

With the fixed N and r, we obtained two sets of six parameters by curve-fitting the Fourier-filtered spectra for the isolated Ni-N interaction. For checking the accuracy of the results from analyses with these parameters, the least-squares fit to the filtered spectrum of each compound was carried out with the set of parameters obtained above for the other compound. The values obtained for N and r are shown in Table 1, which demonstrates that the analysis adopted here gives a reliable structural information.

Then we determined the N and r values for the ammine and the ethylenediamine complexes of nickel(II) in aqueous solutions with both sets of parameters. The Fourier-filtered and the least-squares fit curves are shwon in Fig. 7 for a solution of ethylenediamine nickel(II) nitrate; a set of parameters obtained from the spectrum of solid $[Ni(en)_3](NO_3)_2$ was used in the analysis. The numerical results are summarized in Table 2. Analyses with two different sets of parameters gave results in good agreement with each other. The measured coordination numbers are about six and the measured Ni-N distances are about 2.12 Å for both complexes in solutions. The values for the ethylenediamine complex are close to those for the same complex in the crystals, but are significantly different from that obtained by Fujita *et al.*[6] from their diffraction study on a solution. This inconsistency needs further investigation. Generally speaking, the EXAFS method as applied to solutions has the advantage that it detects only the interatomic interactions in which the nickel atom (or any other atom concerned) is involved, whereas the X-ray diffraction method gives a diffraction pattern which is the superposition of various diffractions by different pairs of atoms at different distances.

TABLE 2. RESULTS OF THE CURVE FITTING ANALYSIS OF THE EXAFS SPECTRA OF AQUEOUS $[Ni(NH_3)_6]^{2+}$ AND $[Ni(en)_3]^{2+}$ SOLUTIONS

	Set of parameters	Coordination number	Ni-N distance/Å
$[Ni(NH_3)_6]^{2+}$	A	6.0±0.8	2.13±0.01
	B	5.7±0.8	2.12±0.01
$[Ni(en)_3]^{2+}$	A	6.1±0.8	2.13±0.01
	B	5.8±0.8	2.12±0.01

A: Parameters derived from the spectrum of solid $[Ni(en)_3](NO_3)_2$. B: Parameters derived from the spectrum of solid $[Ni(en)_3]SO_4$.

The authors (especially M. S.) would like to thank Prof. K. Taniguchi of Osaka Electrocommunication University for his encouraging suggestions and useful discussions.

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