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EXAFS Measurements under High Pressure Conditions Using a Combination of a Diamond Anvil Cell and Synchrotron Radiation

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EXAFS spectra for Fe, Co, Ni K-edges were successfully measured under high pressure conditions using a combination of a set of normal 1/8 carat diamond anvils, synchrotron radiation and a scintillation counter. A newly developed motor controlled goniometer stage was used for adjusting the position of a miniature diamond anvil cell. On the measurement of Cr and Mn spectra, specially designed thinner diamond anvil was necessary. EXAFS analysis of bis(dimethylglyoximato)nickel(II) at pressures from 1 atm to 5.6 GPa was made.

A combination of the EXAFS method and the diamond anvil high pressure technique is expected to provide useful crystallochemical information concerning the behavior of a specific element in a material under a high pressure condition although previous workers have not obtained satisfactory results.[1-3] Because of the small divergence of the synchrotron X-ray beam, one can obtain a fine parallel beam of desirable size utilizing a simple set of vertical and horizontal slits which can be placed far away from a sample position. Taking this advantage we have designed a sample stage for high pressure EXAFS measurements using a miniature diamond anvil cell for single crystal study[4] mounted on a motor driven goniometer (Fig. 1). The cell position can be adjusted by a remote controller so that a fine X-ray beam passes through a specimen hole (a few hundred micrometers

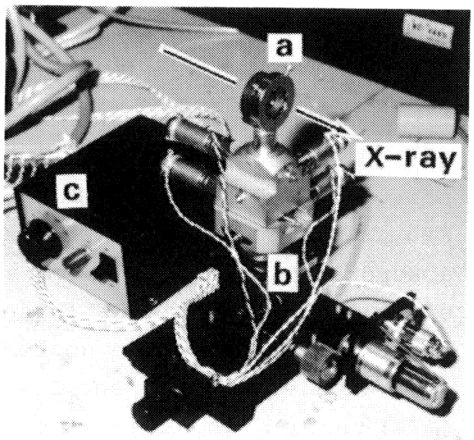

Fig. 1. A view of the sample stage
(a) diamond anvil cell (32.0 mm ϕ)
(b) goniometer with five motors for the two arcs (x,y) and three axes (x,y,z)
(c) remote controller.

in diameter) of a metal gasket of the diamond cell without touching the gasket. This adjustment can be easily made from outside of a radiation proof hutch by monitoring X-ray intensities of the transmitted beam through the cell.

The EXAFS experiments were performed at beam line 10B in the PHOTON FACTORY (PF), Tsukuba, Japan with the synchrotron radiation at an energy of 2.5 GeV. A Si(311) channel-cut monochromator was used for the EXAFS measurements of Ni and Co, and a Si(111) double crystals monochromator was used for those of Fe, Mn, and Cr. The X-ray intensity of the incident beam was monitored by an ion chamber and that of the transmitted beam was measured by another ion chamber for Ni K-edge and by a scintillation counter for Cr, Mn, Fe, and Co K-edges.

Shimomura et al. have reported that the Ga-K edge spectrum was disturbed by Bragg reflections of diamonds in their high pressure EXAFS measurement of GaAs using a diamond anvil cell.[1,3] A similar phenomenon was observed in our experiment (Fig. 2(a)). These absorption spikes owing to the Bragg reflections become a serious problem of data analysis and are a major obstacle of the high pressure EXAFS analysis using diamond anvil cell. The Bragg reflections of diamonds are related with two factors, i.e. a relative orientation of the diamond crystals toward the incident X-ray beam and an energy region of the X-ray used in the measurement. The former effect can be seen in Figs. 2(b) and 2(c), where the positions of absorption spikes significantly changed by a slight tilting of the goniometer arc (0.27° in this case). Therefore, we must find out an optimum orientation of the diamond by tilting the arc prior to the measurement. This adjustment is effective when the number of the spikes is small. In order to examine the latter effect, we have systematically measured EXAFS spectra of several elements started from Ge to those with smaller atomic number, and found that only a few absorption spikes were observed in the regions of Ni, Co, and Fe K-edges. However, it was observed that the intensity of the transmitted beam significantly decreased with decrease in its energy due to the absorption by diamonds. To reduce the absorption it is useful to reduce the thickness of diamonds. So far, we have successfully measured EXAFS spectra of Ni, Co, and Fe (Fig. 2(d)) K-edges under high pressure by using normal 1/8 carat diamond anvils with 3.4 mm in total thickness. The spectra of Cr K-edge (Fig. 2(e)) and Mn K-edge (Fig. 2(f)) have been obtained using diamond anvils with 1.8-mm-thick. Figure 2(f) indicates that Cr K-edge spectrum was seriously disturbed by the absorption spikes. In such a case, we may use XANES instead of EXAFS because the energy region of XANES is so narrow (ca. 100 eV) that the spikes can be easily avoided by tilting the goniometer arc.

We have carried out EXAFS analysis of Ni-dmg (bis(dimethylglyoximato)nickel-(II)) under high pressure conditions up to 5.6 GPa (Figs. 3(a) and (b)). Platy Ni-dmg molecule (Fig. 4) is connected one dimensionally by the Ni-Ni bonding in the crystal structure.[5] Powdered samle was placed in a hole (0.3 mm in diameter) of 0.2-mm-thick metal gasket together with the alcohol mixture as the pressure transmitting medium. Pressures were determined with the conventional ruby fluorescence method. The analysis of spectra was carried out using the program EXAFS1.[6] The EXAFS oscillation curves $X(k)$ were obtained by the least-squares fitting of Victoreen's formula to the pre-edge absorption and background subtraction using the cubic spline technique. Figure 4 shows the Fourier transforms of $k^3\chi(k)$ for Ni-dmg at 1 atm and 5.6 GPa. The phase shifts were not corrected in the Fourier transforms. The strong peaks at around 1.54 Å correspond to the intra-molecular Ni-4N bonds and they show a slight peak shift to short bond

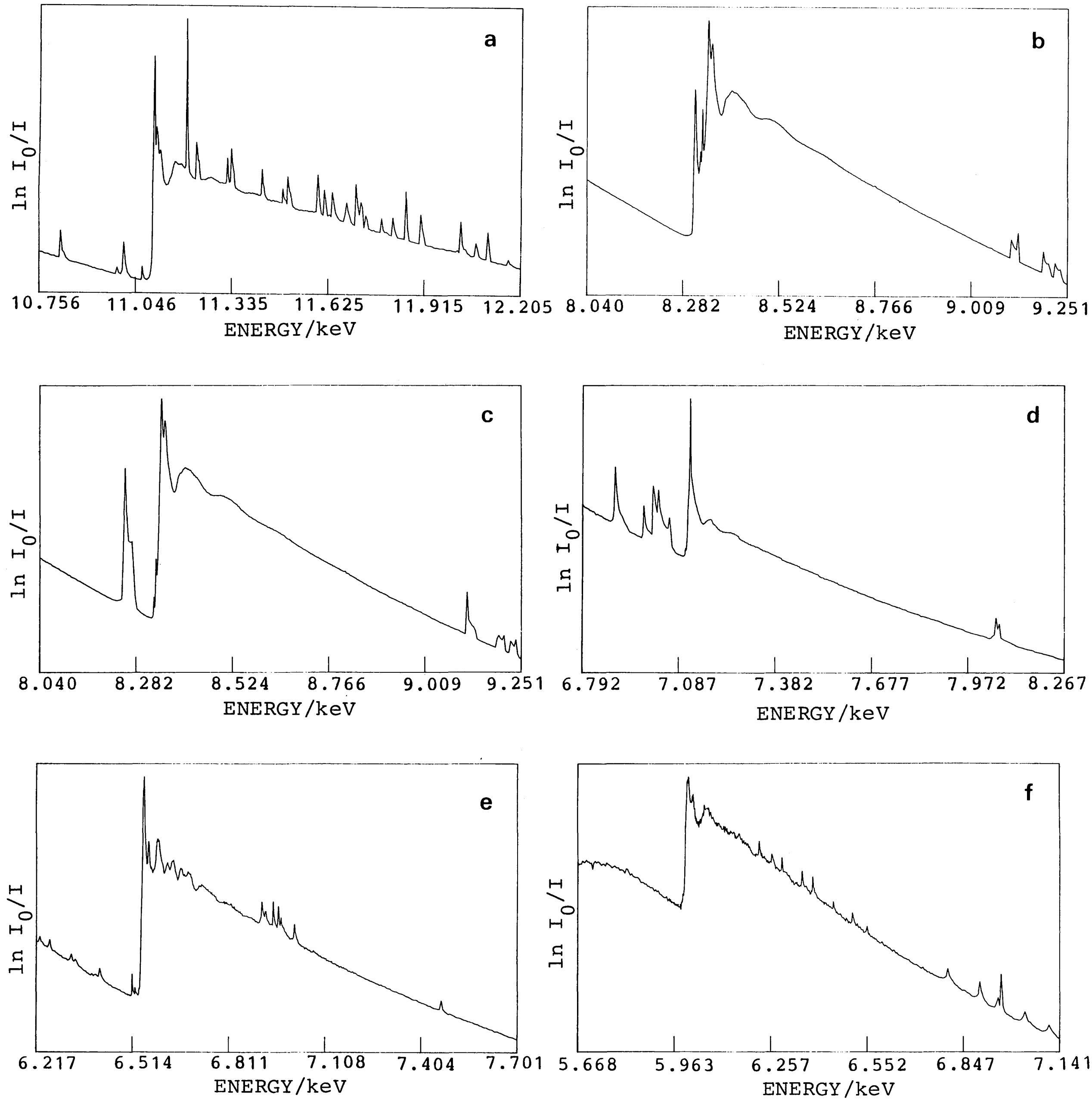

Fig. 2. X-Ray absorption spectra.

(a) Ge K-edge: GeO_2, 1 atm, 1 s/step*.

(b) Ni K-edge: Ni-dmg, 3.4 GPa, 10 s/step, X-arc=2.05°**.

(c) Ni K-edge: Ni-dmg, 3.4 GPa, 5 s/step, X-arc=1.78°.

(d) Fe K-edge: $CuFe_2S_3$, 9.4 GPa, 10 s/step.

(e) Mn K-edge: MnO, 1 atm, 1 s/step.

(f) Cr K-edge: Cr_2O_3, 1 atm, 1 s/step.

* counting time per step; ** tilting angle of the goniometer arc.

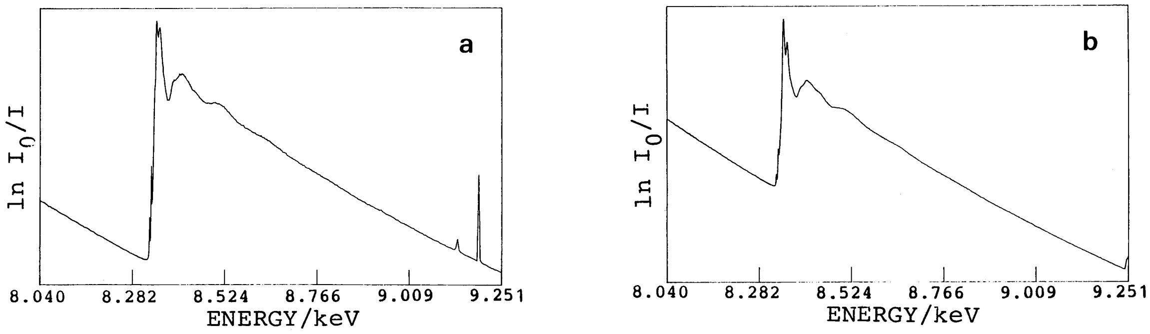

Fig. 3. X-Ray absorption spectra for Ni-dmg: (a) 1 atm, 5 s/step, (b) 5.6 GPa, 10 s/step.

distance with increase in pressure. A comparison of the two curves indicates that several weak peaks above 2.5 Å show large shift and intensity change. Although the Ni-Ni inter-molecular distance is expected to decrease significantly with increase in pressure, the peak corresponding to the Ni-Ni interaction could not be assigned clearly.

As mentioned above, it was necessary to use the diamond anvils of 1.8-mm-thick for the measurements of the EXAFS spectra of Mn and Cr, but obtainable pressure of this cell was not high (<1GPa). We are currently preparing a further experiment using newly designed diamond anvils with minimum allowable thickness for obtaining a higher pressure condition.

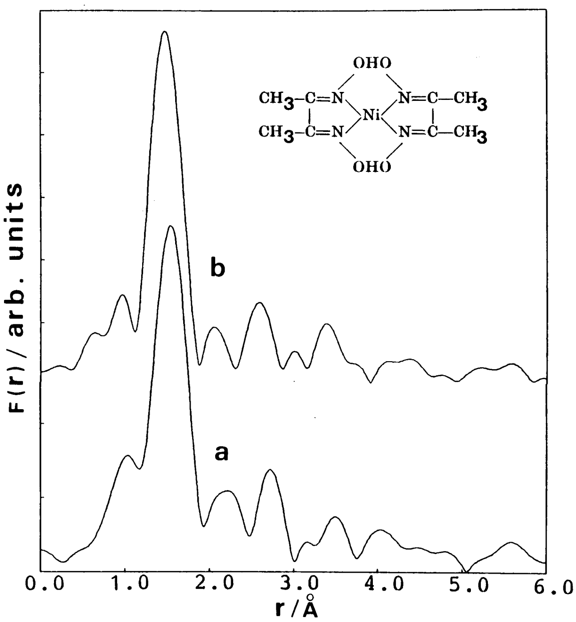

Fig. 4. Fourier transforms of $k^3\chi(k)$ EXAFS for Ni-dmg at (a) 1 atm and (b) 5.6 GPa.

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6) N. Kosugi and H. Kuroda, Program EXAFS1, Research Center for Spectrochemistry, the University of Tokyo (1985); modified version of EXAFS1 by M. Nomura was also used.

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