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EXAFS MEASUREMENT UNDER HIGH PRESSURE BY DIAMOND ANVIL CELL

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Abstract

EXAFS spectra of materials under high pressure were successfully obtained for K-absorption edges of Fe, Co and Ni atoms by making use of synchrotron radiation together with the diamond anvil cell technique. A newly developed goniometer stage with a remote controlled motor was found to be useful for adjusting the position of a miniature diamond anvil cell for an X-ray beam. The present study revealed that an experimental system consisting of a Si(111) monochromator, a scintillation counter and a pair of normal 1/8 carats diamond anvils worked well for the measurement of Fe, Co and Ni atoms. For further measurement of absorption spectra of atoms with lower atomic number than Fe, a specially designed thinner diamond anvil or higher brightness synchrotron radiation source would be required.

Introduction

Although structural studies of crystalline materials under high pressure have been carried out by X-ray diffraction method, it has had still some problems to determine the bond distances or coordination numbers around specific atom in poorly crystallized materials. Owing to the utilization of synchrotron radiation and development of the analytical treatment of the EXAFS spectra, the EXAFS technique has been made widely available to investigate the local structure of the materials whether they are crystalline or not. It was thought to be worthwhile to try to obtain information of local structure under high pressure by coupling a diamond anvil cell and the EXAFS technique. The trial examination on Ni-dmg(Nickel Dimethylglyoxime) and that of cubanite (CuFe_2S_3) were carried out at EXAFS station (BL-10B) of Photon Factory, KEK.

Experimental

Synchrotron radiation was monochromated by Si(311) channel-cut crystal to provide an X-ray beam with the wavelength around K-absorption edge of Ni and Co atoms and by Si(111) double crystals

for Fe, Mn and Cr atoms. The intensity of an incident X-ray beam was monitored by an ion chamber and that of the transmitted beam by another ion chamber for Ni atom, and by a scintillation counter in case of Cr, Fe and Co atoms. The incident beam was made fine (less than 300 μm in diameter) by an aperture and then directed through the hole of the gasket between the diamond anvils. This was achieved by the newly developed goniometer stage with the remote controlled motor to drive X-Y-Z axes. It should be emphasized here that an X-ray beam dose not hit the gasket. A conceivable problems for adopting the diamond anvil to generate high pressure are absorption and diffraction by diamond as in the case reported by one of the authors(0.S)^{1),2)}. The case that EXAFS spectrum is seriously disturbed by Bragg reflection is shown in Fig. 1(a). The occurrence of a Bragg reflection from diamond depends on two factors: a relative orientation of the diamond in an incident X-ray beam and wavelength region of an X-ray used in the measurement. On the former effect, the wavelength of X-ray giving rise to diffraction can be easily shifted by slightly tilting of the goniometer arc of the stage. This case is shown in Fig. 1(b), where the position of the absorption i.e. diffraction by diamond is significantly shifted by a slight tilting of the goniometer arc (0.27° in this case). An optimum orientation of the diamond should be found by tilting the arc prior to the measurement. The adjustment of an orientation is effective when the number of diffraction is small. The latter effect is systematically examined by measuring EXAFS spectra of several elements with atomic number from 24(=Cr) to 32(=Ge). In the region of K-edges of Fe, Co and Ni atoms, a few diffractions from diamond were observed. The intensity of transmitted beam decreased in accordance with the lower atomic number.

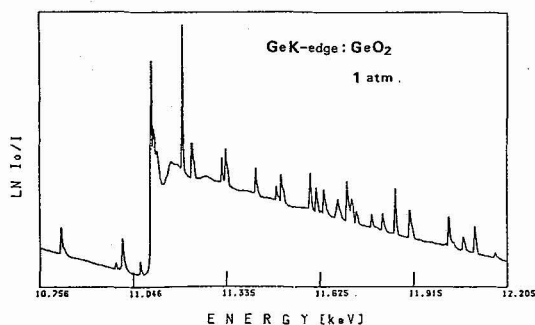


Fig.1(a)

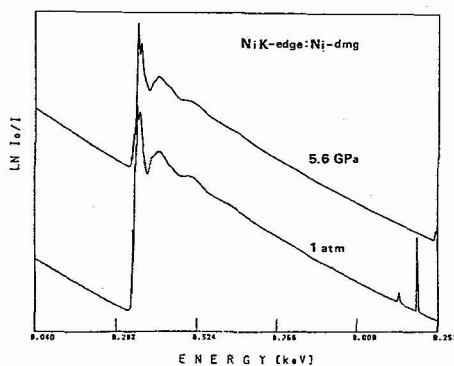


Fig.1(b)

Fig. 1(a). X-ray absorption spectrum of the K-edge of Ge.

There occur many diffractions from diamond disturbing the spectrum.

Fig. 1(b). X-ray absorption spectra of the K-edge of Ni.

Diffractions from diamond shifting their positions in accordance with an arc of goniometer stage.

An examination of several elements in the diamond anvil cell, as mentioned above, revealed that K-absorption edges of elements such as Mn, Fe, Co and Ni were found to be measured by avoiding both

difficulties. At wavelengths longer than the K-edge of Mn, the spectra were seriously affected by both the absorption effect of a pair of 1/8 carats diamond anvils and by Bragg reflection, and at wavelengths shorter than that of the Ni K-edge by Bragg reflection only.

The interim results of the data analysis using the program EXAFS1³⁾ are given below. The EXAFS oscillation curves $\chi(k)$ were obtained by the least-squares fitting of Victoreen's formula to the pre-edge absorption and background subtraction using the cubic spline technique.

Ni-dmg(bis(dimethylglyoximato)nickel(II))

Plane Ni-dmg molecules (Fig. 2) are connected to each other by one dimensional Ni-Ni bonding to form a crystal⁴⁾. It is also known that the compound is changed easily in its Ni-Ni bond distance in accordance with pressure. The absorption spectra were measured at 1 atm., 3.4GPa and 5.6GPa. Those of 1atm and 5.6GPa are shown in Fig. 1(b). The Fourier transform of the spectra at 1atm and 5.6GPa are shown in Fig. 2. The peak at around 1.54 Å corresponds to intra-molecular 4x(Ni-N) bonds which shorten slightly under the effect of high pressure. Although Ni-Ni inter-molecular distance was expected to be clearly shorter, no peak corresponding to the Ni-Ni interaction is discernible in the Fourier transform.

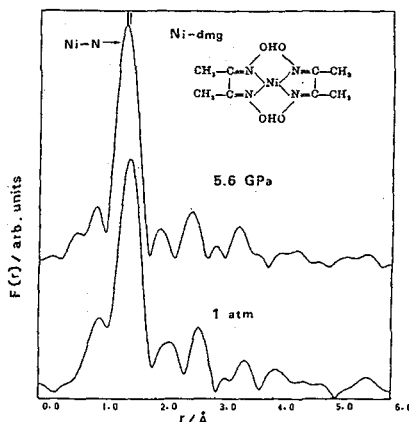


Fig. 2

Fig. 2. Ni-dmg molecule is shown in upper right corner.

The intra-molecular bond distances of Ni-N are shown to be slightly shortened by the effect of pressure.

Cubanite

The copper and iron atoms in orthorhombic cubanite (CuFe_2S_3) are tetrahedrally coordinated in hexagonal close packed array of S atoms. The structure changes to the NiAs type hexagonal form at pressure above 6GPa. The absorption spectra about the K-edge of Fe atom were obtained at 1atm and 9.4GPa and shown in Fig.3. Their Fourier transforms are also shown in Fig. 4 which shows a significant shortening of the Fe-S bonds. A detailed analysis of the data is currently proceeding.

Conclusion

The present study revealed that EXAFS measurements under high pressure using the diamond anvil cell can be performed on materials containing atoms with atomic numbers from 25(=Mn) to 29(=Cu). In future studies, the diamond with minimum allowable thickness combined with strong synchrotron radiation such as might be obtained from a wiggler line or accumulation ring of KEK, may make possible the measurement of the absorption spectra of good quality from materials containing Fe, Mn, Cr, V and Ti atoms.

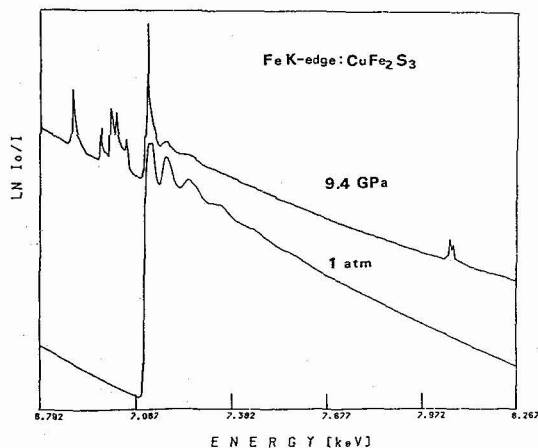


Fig. 3

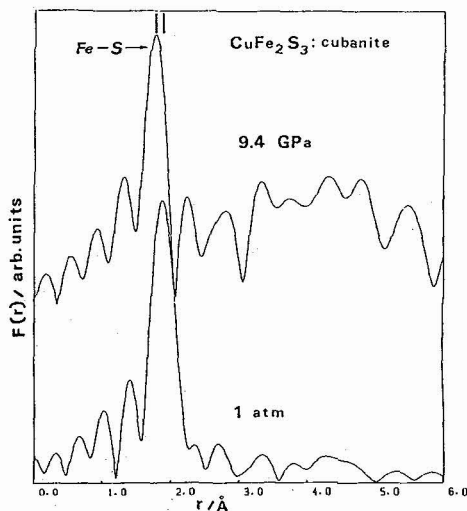


Fig. 4

Fig. 3. X-ray absorption spectrum of the K-edge of Fe.

The spectra at 1 atm was measured without diamond anvil cell.

EXAFS spectrum at both pressures are different to each other without taking account of diffraction from diamond.

Fig. 4. The Fourier transforms of EXAFS spectrum in Fig. 4.

Fe-S bonds are shown to be shortened by the effect of pressure.

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