

A new cell for X-ray absorption spectroscopy study under high pressure^{*}

ZHENG Li-Rong(郑黎荣)^{1,2;1)} CHE Rong-Zheng(车荣征)¹ LIU Jing(刘景)¹
DU Yong-Hua(杜永华)¹ ZHOU Ying-Li(周英丽)¹ HU Tian-Dou(胡天斗)^{1;2)}

¹ (Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China)

² (Graduate University of Chinese Academy of Sciences, Beijing 100049, China)

Abstract X-ray absorption fine structure (XAFS) spectroscopy is a powerful technique for the investigation of the local environment around selected atoms in condensed matter. XAFS under pressure is an important method for the synchrotron source. We design a cell for a high pressure XAFS experiment. Sintered boron carbide is used as the anvils of this high pressure cell in order to obtain a full XAFS spectrum free from diffraction peaks. In addition, a hydraulic pump was adopted to make in-suit pressure modulation. High quality XAFS spectra of ZrH₂ under high pressure (up to 13 GPa) were obtained by this cell.

Key words high pressure, XAFS, boron carbide

PACS 61.05.Cj

1 Introduction

Pressure is a fundamental thermodynamic variable which has an important impact on structures and the functions of materials. Under pressure, the material's physical, chemical and mechanical properties change only because the materials' structure is changed. So we can obtain the relevant information between the structure and properties by using the high pressure method. For the last few decades, structure research under high pressure has become more and more important in condensed matter and geosciences^[1, 2].

X-ray diffraction (XRD) using synchrotron radiation is a significant method to study the material's pressure-induced phase transition and equation of state (EOS), which has been widely used to investigate structures under high pressure. However, using XRD it is hard to get the structural information while materials or phases are amorphous such as liquid and glassy. X-ray scattering (radial distribution function) can make up for this defect to some extent. But it is difficult to apply it to complex systems.

XAFS is a powerful tool for the investigation of the local structure environment around a selected specific atom. XAFS results from the interference between the outgoing photoelectron wave from the X-ray absorbing central atom and the back-scattered photoelectron waves from neighboring atoms^[3]. The information for the local structure around the absorbed atom, such as bond length, bond angle, coordination number, coordination atom's species, etc. can be obtained by XAFS. As its local characteristic, it can deal with complex systems (crystal, quasi-crystal, amorphous, dilute, gas and cluster containing a large number of elements). Besides, using the transition rules and space symmetry during X-ray absorption, XAFS can also be applied to study electronic structure (the hybridization of electronic orbital's, electron transport and transfer). Because of these unique advantages, XAFS has been widely used in condensed matter, material science, chemistry, geosciences, environment, and biological science, etc. Combining XAFS and high pressure techniques can help us to study the local structure of all kinds of materials under high pressure including molten metals^[4].

Received 1 November 2008

^{*} Supported by National Natural Science Foundation of China (10575117)

1) E-mail: zhenglr@ihep.ac.cn

2) E-mail: hutd@ihep.ac.cn

©2009 Chinese Physical Society and the Institute of High Energy Physics of the Chinese Academy of Sciences and the Institute of Modern Physics of the Chinese Academy of Sciences and IOP Publishing Ltd

2 Experimental apparatus

In high pressure research, the device which generates pressure is the basis. Since the 1960s', a lot of high pressure experiment devices have been developed for different methods. Diamond anvil cell (DAC) is most widely used. But diamond which is the single crystal will produce diffraction peaks which bring some problems to XAFS. In this work, we designed a high pressure cell for XAFS which uses sintered boron carbide as the anvil driven by a hydraulic pump.

XAFS spectroscopy is the relationship between the sample's absorption coefficient (μ) and the injection photon energy (E). We can acquire the XAFS signal ($\chi(k)$) from the data process of $\mu(E)$. In transmission mode (Fig. 1), the absorption coefficient μ is defined as $\mu(E) = -\frac{\ln(I/I_0)}{x}$, I_0 is the intensity of the injected X-rays; I is the intensity of the X-rays after passing through the sample; x is the sample's thickness.

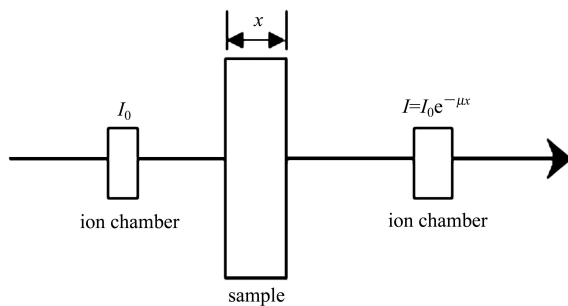


Fig. 1. X-ray absorption experiment in transmission mode.

In the HPXAFS (High Pressure X-ray Absorption Fine Structure) experiment, the sample chamber which generates high pressure is essential. DAC is the most widely used device in high pressure experiments. But in HPXAFS, the diamond anvils which are single crystals will produce a lot of diffraction when the injection X-rays energy meets the Bragg equation. It means that quite a lot of X-rays passing through the diamond anvils will exit in different diffraction angles from the incident direction. So some of them can't be collected by the second ion chamber. Then the signal detected by the second ion chamber changes sharply at these specific energy points when diffractions happen. Finally, these diffraction peaks are added in the XAFS spectrum. It makes the XAFS data hard to analyze. Although by changing the angle between the

DAC and the injection X-rays, some extent of diffraction peaks can be avoided. It is almost impossible to avoid all of this to get clean XAFS data^[5]. Fig. 2 shows the XAFS spectra for YNO_3 under 1.6 GPa collected at BSRF-1W1B using the DAC. It is clear that the diffraction peaks disturb the XAFS spectrum greatly.

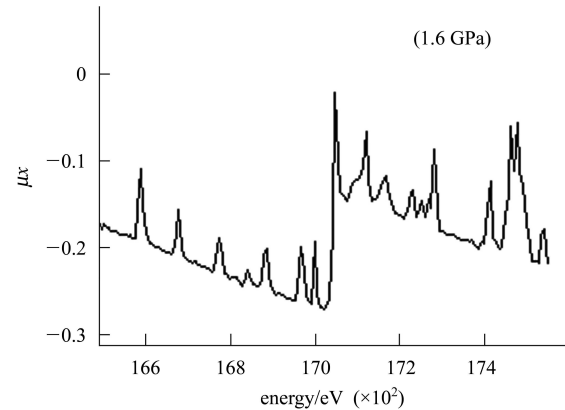


Fig. 2. XAFS spectrum of YNO_3 under 1.6 GPa by DAC.

There are two ways to solve this problem completely. One is to make the incident X-rays through the gasket^[6]. The other is to utilize amorphous or polycrystalline material as the anvils^[7]. In the first method, the X-rays need to be focused to 5 μm and pass through the Be or amorphous boron gasket instead of the diamonds. This method has a high demand on the X-ray focusing and sample position adjustment which are hard to meet at Beijing Synchrotron Radiation Facility (BSRF). So we prefer to use the second method to solve the diffraction peaks in BSRF. The materials of anvil should have enough hardness to endure the great load to generate high pressure. Besides, the X-ray absorption of the anvil should be as small as possible so that there is enough flux for the XAFS experiment. Sinter boron carbide is the hardest material after cubic boron nitride and diamond. Their Moss hardness is about 9.36 GPa, 9.7 GPa and 10 GPa respectively. And its absorption rate to X-rays is about 25% lower than diamond's (75%) when their thicknesses are 5 mm. So it is a suitable anvil material for HPXAFS with the advantages of low cost, easy processing and low absorption to X-rays.

The design of the high pressure cell is shown in Fig. 3. Except for the tungsten carbide seat and SS304 thick-film capillary, all the other parts are made from 40Cr stainless steel. For the alignment of the anvil, four mutual perpendicular windows are opened in the shell through which the anvils can be aligned perfectly by the spherical seat. In addition,

in order to satisfy the requirement of angle for XRD, the exit of 24 degrees has been kept from the sample to the back stop.

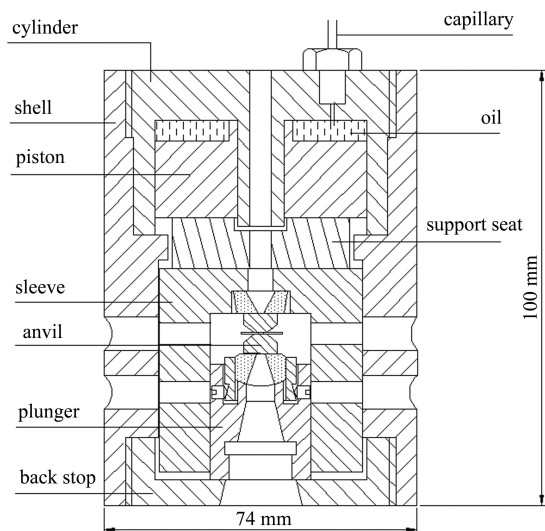


Fig. 3. The schematic diagram of the high pressure apparatus.

We tried two culet designs, the 3 mm flat culet and the 1.6 mm bevel angle culet. The flat one was broken at 3 GPa while the bevel one with different diameters could reach 13 GPa in HPXAFS experiment.

A manual hydraulic pump was used to provide the load for the cell. The oil was squeezed into the thick-film capillary in order to transfer the load to push the piston cylinder pressing the boron carbide anvils. There are several advantages to using this external load mode: 1) Easy to carry out in-suit experiment; 2) Because the diameter of the boron carbide anvil is larger than 1 mm, the external load needed to reach the 10 GPa is huge. If we still push the anvils by hand, the screws and the cell have to use stronger

material that is too hard to machine. So we designed a hydraulic pump to do this. 3) The area ratio between the piston cylinder and the anvil culet is about 900, so that the pressure can be controlled precisely; 4) The external load provided by the hydraulic pump is more uniform in the axial direction than manually tightening the screws.

The hydraulic pump can also be easily applied to DAC while replacing the sleeve, piston and platen with DAC. When the oil pressure is 2 MPa and the diamond culet is 0.4 mm, the pressure in the 0.15 mm sample hole is about 40 GPa.

3 High pressure XAFS experiment

To test the performance of this cell, ZrH_2 powders under pressure were studied by XAFS. Zirconium K-edge (17998 eV) XAFS spectra were collected at 1W1B-XAFS, BSRF has a storage ring electron energy of 2.5 GeV, a current of 120 mA and an exit fixed Si(111) double-crystal monochromator. The scanned energy range is 17898–18998 eV. Fig. 4 shows the schematic of the high pressure XAFS. Ion chambers filled with Ar gas were used to monitor the photon flux before and after the sample. The current signals acquired by the ion chambers were amplified by a weak current amplifier (KEITHLEY 427), converted into voltage signals, sent to scalar (ORTEC 974) through voltage frequency conversion and processed by the computer to acquire the XAFS data.

The gasket is a 0.6 mm thick 40Cr steel, pre-indented to 0.25 mm, with a 0.6 mm sample hole. The sample was uniformly mixed with the graphite to give a suitable μ_x . Every spectrum was measured after loading to ensure that the oil pressure was stable.

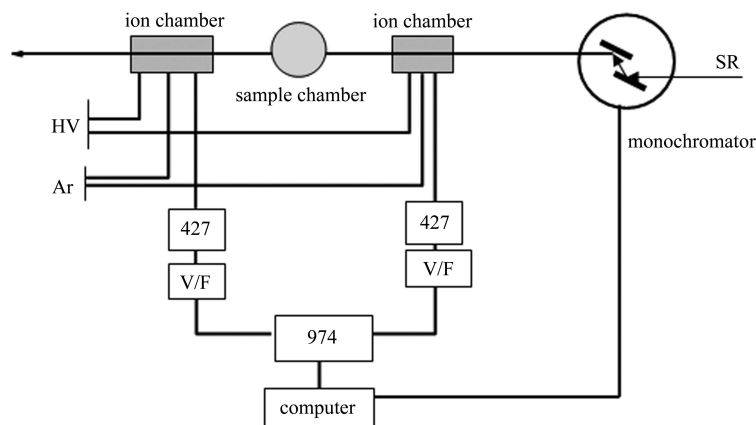


Fig. 4. Scheme of high pressure XAFS experiment.

The boron carbide is black so that the pressure calibration cannot employ the ruby-fluorescence method. To get the approximate pressure, we compare the sample's nearest and next-to-nearest bond distance of samples obtained by XRD and XAFS. Angular dispersive XRD experiments using DAC were performed at the 4W2 High Pressure Experimental Station of BSRF. The anvils culet is 400 μm and the sample hole is about 200 μm drilled in a T301 stainless steel pre-indented to 30 μm . The diffraction patterns were recorded on the MAR345 image plate. The same powders with two ruby chips, 20–30 μm , as the pressure calibration were used.

4 Results and discussion

Figure 5 shows the Zirconium K-edge XAFS spectrum of ZrH_2 under different pressures. It is easy to see that there are no diffraction peaks in the full energy range.

The XAFS signal, $\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}$, can

be obtained after background subtraction, absorption edge determination, E - K conversion ($k = \sqrt{2m/\hbar^*(E - E_0)}$), and atomic absorption coefficient μ_0 subtraction. Fig. 6(a) and (b) show k^2 -weighted $\chi(k)$ and the Radial distribution function $|F(r)|$. $F(r)$ is obtained by Fourier transform of k^2 -weighted $\chi(k)$.

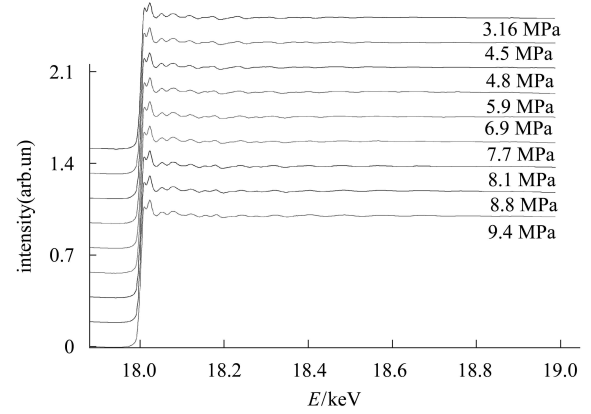


Fig. 5. XAFS spectra of ZrH_2 under different oil pressures.

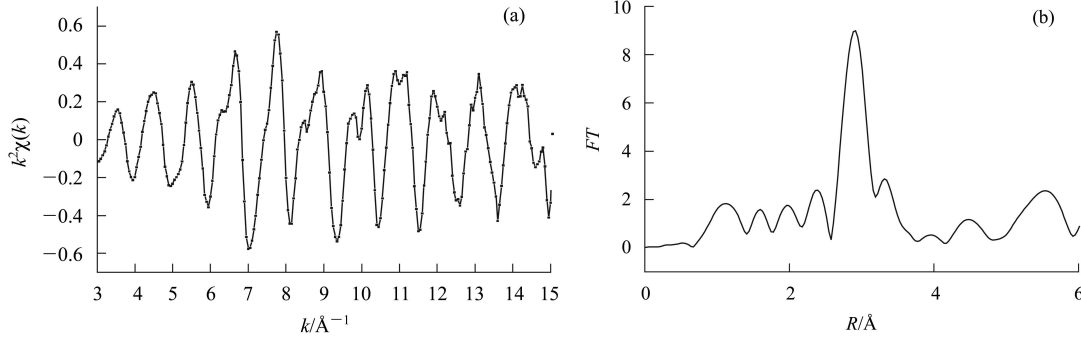


Fig. 6. (a) k^2 -weighted $\chi(k)$ of the ZrH_2 under 4.8 MPa oil pressure; (b) Fourier-transformed XAFS spectrum of the ZrH_2 under 4.8 MPa oil pressure.

As mentioned above, the boron carbide is black so the ruby-fluorescence method is not suitable here. But we can mix some standard pressure calibration materials with the sample. Then we can compare the bond length of the calibration material obtained by the XRD data which can use the ruby-fluorescence method and the XAFS data respectively. Finally we can ascertain the pressure between the boron carbide anvils.

In this work, we got the lattice parameter of ZrH_2 by XRD under pressure calibrated by ruby fluorescence first. After that we measured the XAFS spectrum of ZrH_2 in this cell which used boron carbide anvil. Then, we compared the nearest and the near-

to-nearest bond lengths obtained by these two methods to determinate the pressure in the sample hole.

Figure 7(a) and (b) show the change of the two neighbors Zr-Zr bond length under pressure obtained from ADXRD and XAFS respectively. We can obtain the highest pressure, 13 GPa, which our cell reached by comparing these data.

As the area ratio between the piston cylinder and the culet is 900 in the cell, if the oil pressure is 1 MPa, the pressure at the culet is about 0.9 GPa. Because the sample hole is at the center of the culet, the pressure is larger than 0.9 GPa. The relationship between the oil pressure and the pressure in the sample hole has been obtained by fitting the experimental data.

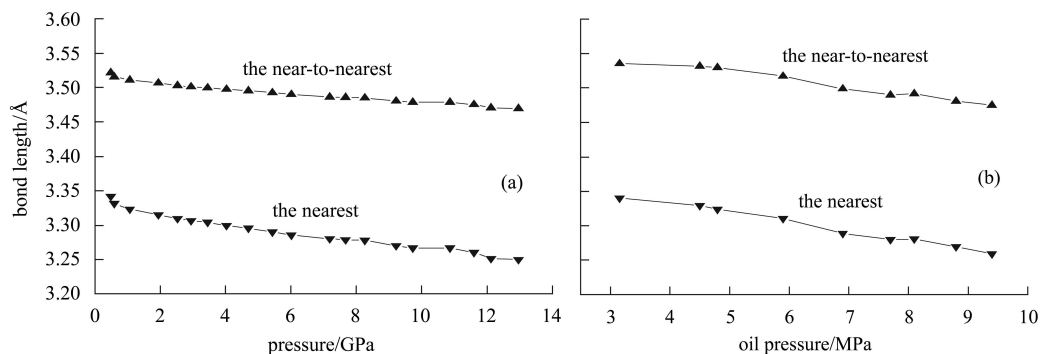


Fig. 7. (a) The two neighbors Zr-Zr bond length under pressure obtained by ADXRD; (b) The two neighbors Zr-Zr bond length under pressure obtained by XAFS.

$$P_O = 0.47P_R + 0.32; \quad P_R = 2.13P_O - 6.8;$$

where P_O (MPa) is the oil pressure, and P_R (GPa) is the pressure in the sample hole.

The problem of zero shift might be caused by the sample hole not being filled in the preparation.

5 Conclusions

We obtained a good signal-to-noise ratio XAFS spectrum of ZrH_2 under high pressure up to 13 GPa by using high pressure apparatus with boron carbide anvils, which is driven by hydraulic pump. It is a good start for HPXAFS study at BSRF that provides a new method to investigate the materials' atomic and electronic structure under high pressure.

References

- 1 Mujica A, Munoz A, Rubio A, Needs R J. *Rev. Mod. Phys.*, 2003, **75**: 863
- 2 Katayama Y, Tsuji K. *J. Phys.: Condens. Matter*, 2003, **15**: 6085
- 3 Koningsberger D, Prins R. *X-ray absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*. New York: John Wiley and Sons Inc., 1988
- 4 Soldo Y, Hazemann J L et al. *Phys. Rev. B*, 1999, **57**: 258
- 5 Itié J P, Baudalet F et al. *J. Phys.: Condens. Matter*, 2005, **17**: S883
- 6 MAO Ho-Kwang, SHU Jin-Fu, SHEN Guo-Yin et al. *Nature*, 2003, **396**: 741
- 7 Houser B, Ingalls R. *Phys. Rev. B*, 2000, **61**: 6515