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The measurement of differential EXAFS modulated by high pressure

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Differential EXAFS (DiffEXAFS) is able to detect subtle atomic perturbations in the local area of the absorbing atom. Here a new method of performing DiffEXAFS experiments under the modulation of high pressure has been developed. Periodic pressure was achieved in the gasket with the help of a dynamic diamond anvil cell, and the measurements were conducted in common energy-scanning mode. This technique has been utilized on ZnSe at 4.8 GPa. The present results have demonstrated a good agreement with the equation of state of ZnSe, and revealed sensitivity to atomic displacements of one order higher in magnitude than that of conventional EXAFS.

Keywords: differential EXAFS; DiffEXAFS; high-pressure modulation; dynamic DAC.

1. Introduction

X-ray absorption fine structure (XAFS) probes the local electronic and lattice structure surrounding the selected absorbing atoms (Sayers *et al.*, 1971; Stern, 1974; Rehr & Albers, 2000). As a short-range structural probe, XAFS places few constraints on the samples and can be used in a variety of systems. It is especially attractive for studying disordered materials, as well as for carrying out *in situ* investigations of dynamical processes. Recently the modulation technique has been applied to XAFS experiments to study the small structural changes under external fields. The spectrum modulated by the periodic perturbation of external fields is always connected to the differential spectrum, so it can substantially increase the contrast of microstructures that are difficult to discover on the static spectrum. Owing to the unique characteristic of high resolution and high sensitivity, various modulation methods have been developed to study the spectroscopy of semiconductors since the 1960s (Seraphin & Bottka, 1966). At the end of the 20th century the technique was also introduced into the XAFS experiments, such as light-modulated XAFS spectroscopy (Suzuki *et al.*, 2001; Okamoto *et al.*, 2003) and differential extended X-ray absorption fine structure (DiffEXAFS).

DiffEXAFS, an attractive technique established by Pettifer *et al.* (2005), can detect subtle changes in absorption fine structure induced by the modulation of a given sample property of interest. So far, magnetic DiffEXAFS (Pettifer *et al.*, 2005; Pascarelli *et al.*, 2007) and thermal DiffEXAFS (Ruffoni *et al.*, 2007*a*) have been observed. The results from these researches indicate that DiffEXAFS is able to explore femtometre-scale atomic displacements, and shows a sensitivity of 100 times better than non-modulated static EXAFS spectra.

However, the modulation of high pressure, another important thermodynamic parameter, has not yet been applied to DiffEXAFS to our knowledge. Here pressure-induced DiffEXAFS is presented, measuring EXAFS changes caused by periodically modulated pressure on the sample. The study of phase structure under high pressure is one of the main themes in condensed matter physics (Jayaraman, 1983). High-pressure EXAFS has offered an important local structural tool (Ingalls *et al.*, 1978; Freund *et al.*, 1989; Di Cicco *et al.*, 1996; Wang & Ingalls, 1998). In this paper we have developed a new method for carrying out higher-resolution EXAFS measurement for high-pressure physics research. Experiments were completed in energy-scanning mode, and DiffEXAFS spectra were obtained at the Zn *K*-edge upon several dynamic pressure ranges at 4.8 GPa. We currently have shown a sensitivity to mean atomic displacements of one order higher in magnitude than that of traditional EXAFS techniques.

2. Experiment details

2.1. Pressure modulation system

In order to perform pressure-modulation DiffEXAFS, it is necessary to exert a time-dependent load on the sample. A pressure modulation system was built up on the basis of a dynamic diamond anvil cell (dDAC), as shown in Fig. 1(*a*). The dDAC, recently developed by Evans *et al.* (2007), can be used for precise and tunable control of pressure in the gasket. It is an important advance in high-pressure experimental science. The device allows time-resolved study of the kinetics of pressure-induced phase transitions and dynamic phenomena, such as the processes of crystallization and growth (Lee *et al.*, 2006, 2007).

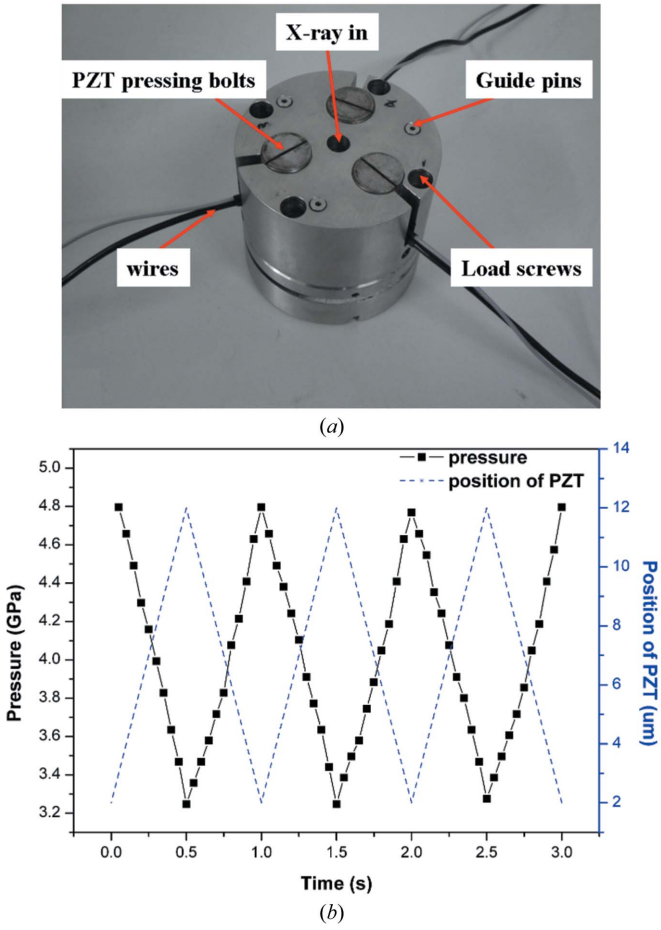


Figure 1
(*a*) Photograph of the dDAC. Three piezo actuators (PZTs) are mounted between two parts of the cell. The pressure between two diamond anvils will change when three PZTs move simultaneously. (*b*) Several periods of pressure change on ZnSe in a dDAC at 4.8 GPa. Solid squares denote the pressure measured by ruby fluorescence. The dashed line is a periodic 1 Hz ramp wave applied to three actuators.

Three piezoelectric actuators (PZTs) were mounted into the dDAC and controlled by a PZT driving system that could be set to a specific wave form. The driving system offered a high-accuracy closed-loop operation, and allowed direct control of the position of the actuators with a precision of 0.3 nm. Under the high-accuracy position controlling, three actuators would move almost simultaneously all the time to avoid producing extra stress in the gasket.

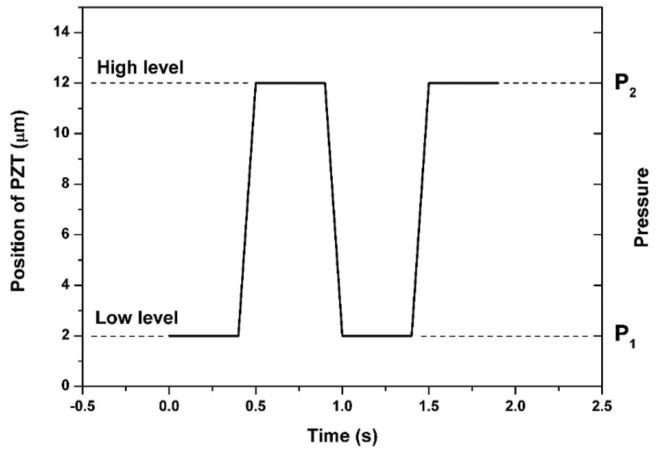
The distance between two diamond anvils in the dDAC was modulated by the periodic motion of the PZT, and then the pressure on the sample varied with the small adjustment of the distance. The pressure would drop when the actuators stretched out. The relation between the pressure change of the sample and the position of the actuators was tested using the ruby fluorescence method (Forman *et al.*, 1972). The diamond culet we used was 400 µm and the sample chamber dimensions were Ø180 × 35 µm in a T-301 stainless steel gasket, where ZnSe powder was loaded as the sample and silicon oil as a pressure-transmitting medium. Load screws were first tightened to reach an expected initial pressure of interest. Then actuators were mounted and enclosed using the pressing bolts. The displacement range of each actuator was 0–15 µm. We set the initial position of the actuators to 2 µm, ensuring a tight touch with the cell. Fig. 1(*b*) shows that the pressure of ZnSe in the dDAC reduced by 1.5 GPa at 4.8 GPa when three actuators extended by 10 µm, and the linearity and repeatability of the system seemed good. It was apparent that the dynamic pressure range depended on the extension length of the PZT, the initial pressure and the stiffness of the sample. For the existence of friction, we only focused on two pressure states, and the error of pressure change maintained no more than 0.02 GPa when the dDAC reached equilibrium under the control of a 1 Hz square wave.

2.2. Measurement method

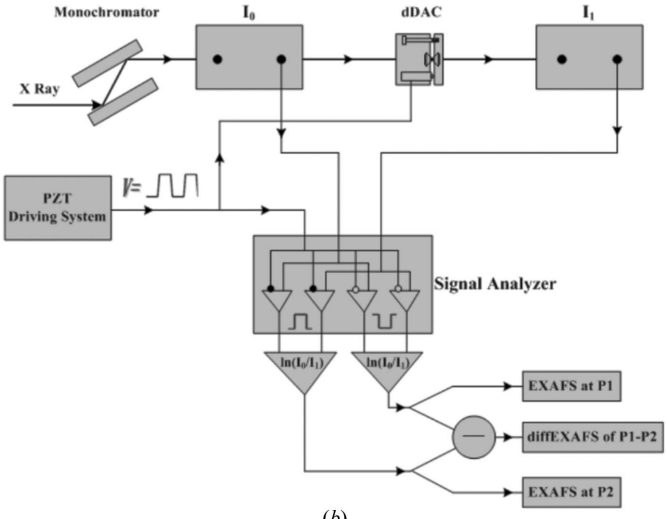
DiffEXAFS is used to measure tiny changes in EXAFS signals between two modulation states. However, the differential signals are usually so weak that the changes are difficult to obtain by a simple subtraction of two EXAFS spectra measured independently in different states, especially for femtometre-scale atomic displacements. There are two main factors that must be taken into account. First, the X-ray energy scale of the two EXAFS spectra should be identical. The energy deviation of every scanning point in the two spectra must be less than 0.1 meV for femtometre resolution (Ruffoni *et al.*, 2007*b*). Any energy drift may introduce errors into the DiffEXAFS. Second, it is crucial to keep the statistical noise as low as possible. Spurious signals can be generated in fine structure from fluctuations of the light source and beamline, such as the instability of intensity and beam spot. Therefore, EXAFS data at two modulation states should be collected within a short time interval to ensure the same external conditions and statistical errors that can be largely eliminated through the difference method. To date, most DiffEXAFS experiments have adopted the energy-dispersive XAFS mode.

In this paper we have designed a new measurement method and used the traditional energy-scanning mode. The configuration of the DiffEXAFS experiment is shown in Fig. 2. A square wave at certain frequency was divided into two parts: one was set to control three PZT actuators in the dDAC, the other was connected to a signal analyzer as a reference signal. The pressure on the sample changed rapidly and periodically between two different states under precise control of the dDAC: the low level of the square wave indicated a higher pressure, and the high level indicated a slightly lower pressure, as shown in Fig. 2(*a*).

The signal analyzer was designed to separate signals immediately into two conventional EXAFS channels according to the level of the square wave: one channel was only for signals of low level to pass; the other was for high-level signals. Then, in each short period, the absorption signals of the two pressure states were measured synchronously, and integrated for a few seconds at the same energy point. Thus two EXAFS spectra were measured simultaneously at one time of the energy scanning, and their difference gave the DiffEXAFS spectrum.



(*a*)



(*b*)

Figure 2
(*a*) Modulation signal of a 1 Hz square wave. The low level corresponds to a pressure P_1 on the sample and the high level to P_2 ($P_1 > P_2$). (*b*) Schematic diagram of a DiffEXAFS measurement. The square wave is divided into two parts: one part controls three PZTs, the other is a reference signal of the signal analyzer. The EXAFS spectra at P_1 and P_2 are obtained simultaneously, and their difference gives the DiffEXAFS spectrum.

Experiments were carried out at the 1W1B station of Beijing Synchrotron Radiation Facility (BSRF) and data were collected at the Zn *K*-edge in ZnSe power. As the structure of ZnSe under high pressure is well known (Smith & Martin, 1965; Greene *et al.*, 1995; Mujica *et al.*, 2003), it is convenient to analyze the experimental results and evaluate the feasibility of the technique. A 1 Hz square wave was used to control the motion of the PZT actuators. When reaching a state of equilibrium, the pressure change in the dDAC was 1.5 GPa at the initial pressure of 4.8 GPa. The results of the measurements are shown in Fig. 3.

3. Analysis and discussion

3.1. Theoretical analysis

Considering small atomic distance changes in the sample, the first-order Taylor expansion is applied to the extended

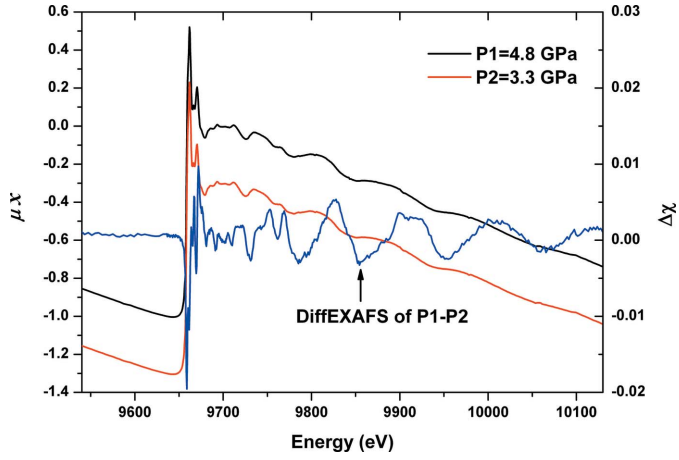


Figure 3
Results of the measurement of Zn *K*-edge DiffEXAFS in ZnSe at 4.8 GPa with ΔP = 1.5 GPa.

absorption fine-structure function (Pettifer *et al.*, 2005; Ruffoni, 2009).

From the simplified EXAFS equation,

$$\chi(k) = \sum_j A_j(k) \sin\left[2kR_j + \varphi_j(k)\right]. \quad (1)$$

Then it can be deduced that

$$\Delta\chi(k) = \sum_j A_j(k) \cos\left[2kR_j + \varphi_j(k)\right] 2k\Delta R_j. \quad (2)$$

In (1) and (2), k is the wavevector of a photoelectron and R_j is the atomic distance of the jth shell around the absorbing atoms. The expression of the differential fine-structure function $\Delta\chi$ sums over all possible scattering paths j, and neglects the R_j-dependence in amplitude $A_j(k)$ and phase $\varphi_j(k)$, for changes in these parameters are much smaller compared with ΔR_j.

There are some differences between the differential signal and the non-modulated EXAFS signal. First, the differential signal has an additional k weighting and 90° phase shift. Second, the amplitude of the signal is proportional to the average displacement of each shell that can be extracted from the fitting.

3.2. Results and discussions

DiffEXAFS spectra of the Zn *K*-edge in ZnSe were studied upon various pressure differences ΔP (Fig. 4). The frequency of the square wave was 10 Hz. ΔP depended on the amplitude of the PZT with an error of less than 0.01 GPa. The normalized EXAFS spectrum at 4.8 GPa is also shown at the top of the figure. It is easy to find 90° phase shifts between the traditional EXAFS and the DiffEXAFS.

According to the Birch–Murnaghan equation of state of ZnSe from X-ray diffraction experiments (Karzel *et al.*, 1996), the pressure dependence of the first coordinated Zn—Se bond length is almost a straight line with a slope of 0.01 Å GPa^{-1} below 5 GPa. We have fitted the first coordinated Zn—Se shell using equation (2) to extract the atomic distance changes ΔR (Ruffoni *et al.*, 2008; Ruffoni & Pascarelli, 2009), using the

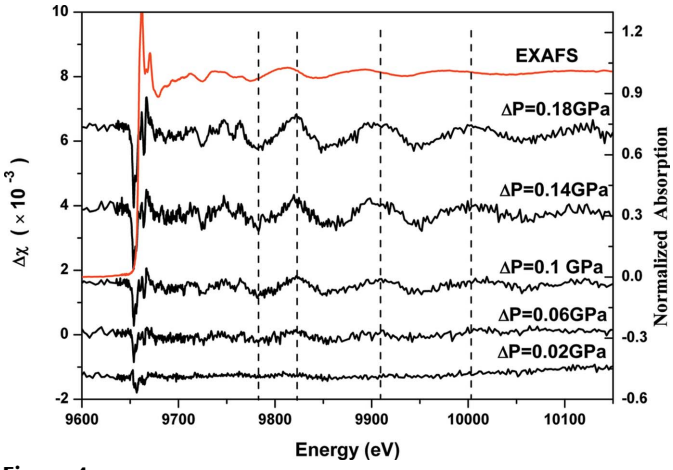


Figure 4
Zn *K*-edge DiffEXAFS signal upon various pressure differences. The initial pressure is 4.8 GPa. The (red) line at the top is the normalized EXAFS spectrum of the Zn *K*-edge in ZnSe at 4.8 GPa.

programme *IFEFFIT* (Newville, 2001). The amplitudes $A_j(k)$ and phases $\varphi_j(k)$ can be determined from the conventional EXAFS spectrum at 4.8 GPa. When these structural parameters are known, it is helpful to analyze equation (2). Fig. 5 shows the fitting results of the theory to experiment for the first shell of ZnSe DiffEXAFS data. The fitting errors are plotted in Fig. 5(*b*) and the black solid line is deduced from the equation of state of ZnSe. By comparison it has shown that they are in good agreement with X-ray diffraction experiments, proving the feasibility of the technique.

In fact, it is a challenge to detect weak DiffEXAFS signals under high pressure (Ingalls *et al.*, 1980; Hong *et al.*, 2009). Firstly, the diamond anvil cell, which is used to generate high pressure, reduces the X-ray intensity by about one to two orders of magnitude owing to the absorption of diamonds. Secondly, Bragg diffraction peaks of the single-crystal diamonds can cause problematic glitches which disturb the EXAFS spectra. However, this situation is sometimes avoided by optimizing the position of the cell and of the two diamonds. Finally, BSRF is a first-generation synchrotron radiation source and its brightness is much lower than that of advanced third-generation sources. It can be found from Fig. 4 that the difference signals become lost when ΔP is below 0.1 GPa. Considering the signal-to-noise ratio, the technique is sure to be able to resolve atomic displacements modulated by pressure to an accuracy of at least 0.1 pm, *i.e.* 100 fm.

4. Summary

Pressure-modulated DiffEXAFS have been developed in a dDAC and using energy-scanning mode. The method is quite simple and easy to be applied to other modulation techniques, such as temperature modulation, light modulation, electric field modulation and so on. It can expand the application range of DiffEXAFS. With a limited source intensity and the absorption of two diamonds, we have still detected atomic displacements of at least 100 fm. It is possible to achieve femtometre order by using a higher-brightness light source and thin diamond anvils. Combined with the dDAC technique and the EXAFS method, pressure-modulated DiffEXAFS may develop into an important local structural tool for the high-resolution and detailed investigation of the kinetics of transitions under high pressure, especially in non-crystalline material.

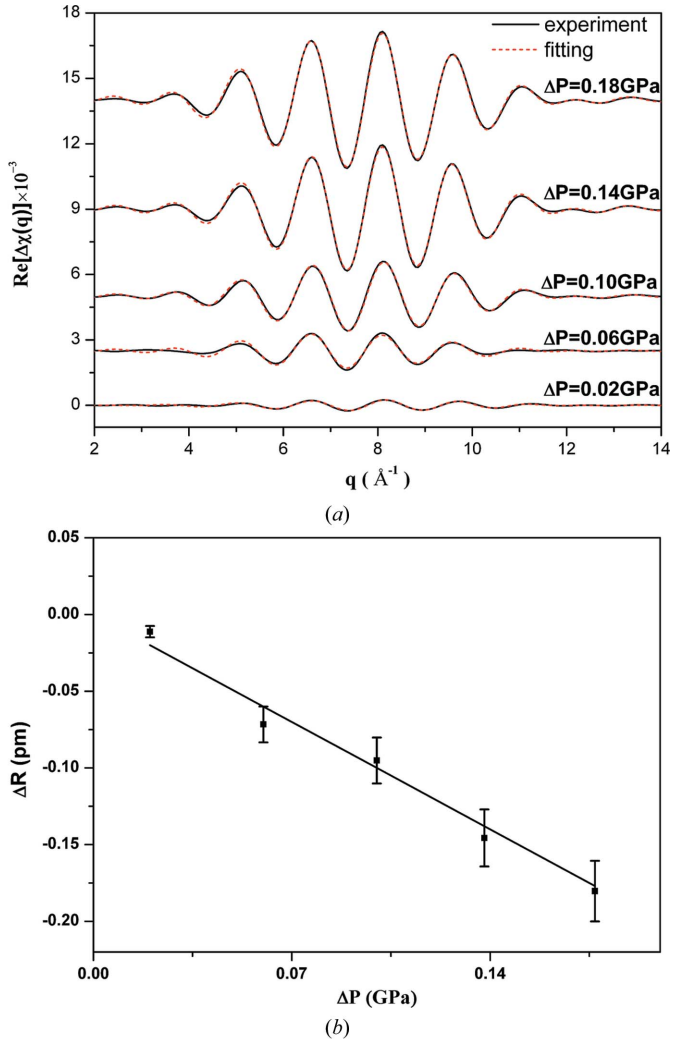


Figure 5
(*a*) Fitting results of DiffEXAFS data with different ΔP. (*b*) The solid line is deduced from the Birch–Murnaghan equation of state of ZnSe. The negative value of ΔR denotes a reducing bond length with increasing pressure.

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