Development of pressure-modulated EXAFS method*

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Abstract: Many modulation techniques have been widely applied to improve the quality of conventional spectra. Here a pressure-modulated EXAFS method is proposed to detect the small changes of local structure induced by the modulation of high pressure. In the experiment a dynamic diamond anvil cell was used to put a periodic load on the sample and lock-in amplifier to measure the modulated EXAFS signals. We have applied this technique to ZnSe and revealed a sensitivity to atomic displacement of 0.1 pm that is about ten times better than that of traditional EXAFS.

Key words: modulated EXAFS, modulation, high pressure, dynamic DAC

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1 Introduction

A modulated spectrum is used to detect small changes of optical reflection and absorption induced by the modulation of a given sample property. Many modulation techniques have been widely applied in the area of semiconductor spectroscopy, and some have been introduced into XAFS experiments, such as wavelength [1], light [2], magnetic field [3], temperature [4] and so on. In this paper the pressure-modulated Extended X-ray Absorption Fine Structure (EXAFS) is presented, measuring subtle changes in EXAFS signals caused by the modulation of high pressure. Pressure compresses atomic distances, and leads to changes in the photoelectron scattering path length around central absorbing atoms that can be measured by EXAFS. However, traditional EXAFS is only able to resolve atomic displacement to 0.01 Å. Modulated EXAFS can detect femtometer-scale atomic displacements, about 100 times more sensitive than static EXAFS.

We have developed a measurement method of pressure-modulated EXAFS and applied this technique to a sample ZnSe. The results show good agreement with X-ray diffraction experiments, demonstrating the viability of the technique. Pressure-modulated EXAFS has combined the EXAFS method, modulation technique and high pressure condition to offer a new local structural tool for high pressure research.

2 Theory

Given that the changes of atomic distances are small, the modulated fine structure function can be written in the following simplified form Ref. [1]:

$$\Delta\chi=\sum_j A_j(k)\cos(kS_j+\Phi_j(k))k\Delta S_j. \qquad (1)$$

In Eq. (1), $\Delta\chi$ sums up all possible shells contributing to the differential EXAFS. k is the photoelectron wave vector, A_j and Φ_j are the amplitude and phase respectively of the j-th scattering shell. S_j is the path length and equals $2R_j$, and R_j is the distance of the j-th shell from the absorbing atom. According to Eq. (1), it is possible to obtain the information of mean atomic displacement ΔR_j from the fitting [5].

3 Experiments

Two problems should be solved before experiment: one is how to obtain modulated pressure; the

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other is how to measure the modulation signals.

First, a dynamic diamond anvil cell (dDAC), a novel device developed by Evans et al. [6], was used to exert a modulated pressure on the sample, as shown in Fig. 1. Three Piezoelectric Transducer (PZT) actuators were installed between two diamond anvils and controlled by the PZT driven system that could generate various waveforms. The device utilized the periodic motion of the PZT to change the pressure in the gasket.

EXAFS signals of the sample would vary periodically with the pressure that was modulated by dDAC. And Lock-in Amplifier (LIA) was used to extract the modulated EXAFS signals induced by the changing pressure. LIA has a good performance on recovering weak periodic signals that are buried in noise. It requires a reference signal at the same frequency as the measured signal and uses this to demodulate the input signal. Because of its good ability to overcome noise, the LIA has been widely applied in modulation techniques [7].

Figure 2 shows the entire pattern of the experimental measurement. The PZT driving system generated a sine wave at a certain frequency that was set to control the motion of actuators in dDAC, and at the same time linked to the LIA as the reference signal. The dDAC device was assigned to produce periodic pressure on the sample, which would result in the simultaneous variation of the transmitted X-ray beam (I_1). Then LIA was applied to pick up the weak modulated signals (ΔI_1) from noise. If the changes of EXAFS signals are small, then ΔI_1 can be expressed as follows:

$$\begin{aligned} \Delta I_1 &= \Delta(I_0 \mathrm{e}^{-\mu t}) \approx I_1 \Delta(-\mu t), \\ \text{then } \Delta \mu t &= -\frac{\Delta I_1}{I_1}, \end{aligned} \tag{2}$$

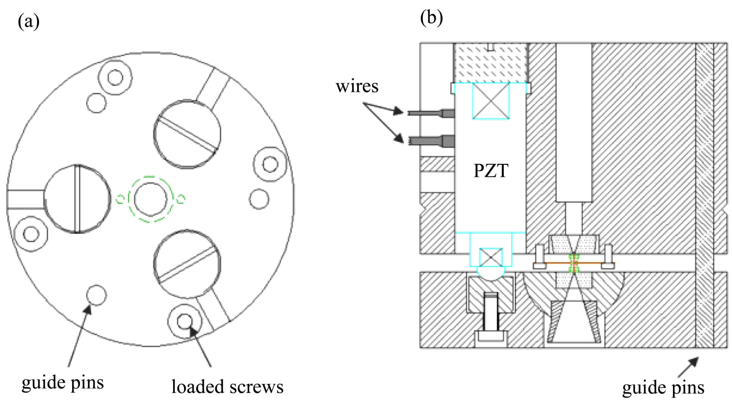

Fig. 1. A schematic diagram of dDAC: three piezo actuators (PZT) are installed between two parts of the cell and controlled by a PZT driving system. The pressure on the sample will change with the motion of the PZT. (a) End-on view; (b) Cross-sectional view.

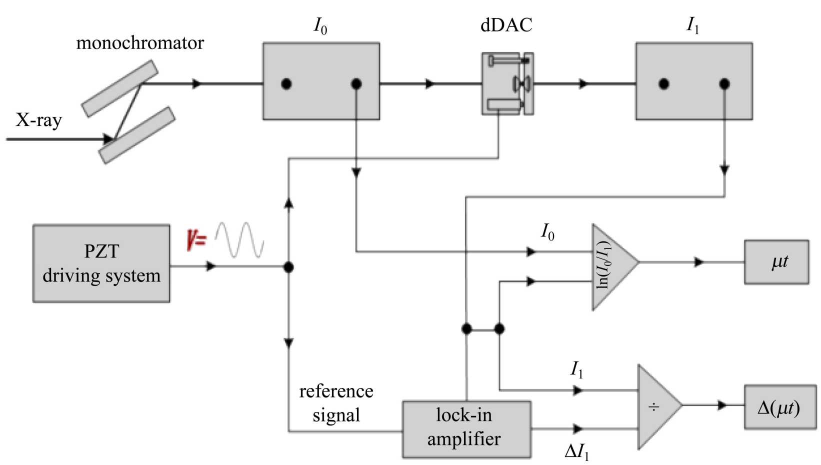

Fig. 2. The pattern of measuring modulated EXAFS. The PZT driving system generates a sine wave as the input signal of the PZT actuators in dDAC and the Lock-in Amplifier. The modulated absorption signals are extracted by the Lock-in Amplifer.

where I_0 is the incident X-ray intensity, $\Delta\mu$ represents the differential X-ray absorption coefficient, t is the sample thickness whose change with pressure is slight and can be neglected if the modulation is sufficiently small. So a modulated EXAFS spectrum can be calculated from Eq. (2).

Experiments were performed at the 1W1B station of the Beijing Synchrotron Radiation Facility (BSRF). ZnSe powder was taken as the sample. First we tightened the dDAC to reach an initial pressure of 5 GPa, then gave a 10 Hz sine wave to the PZT actuators. The amplitude of the pressure change on ZnSe in dDAC was 0.12 GPa that was measured by a ruby fluorescence method [8]. Finally data were collected at Zn K edge in the energy scanning mode. The results are shown in Fig. 3.

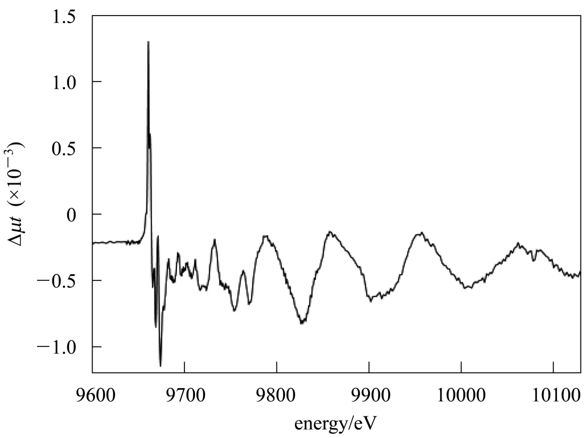

Fig. 3. Experimental results of the modulated EXAFS at Zn K edge. The initial pressure in dDAC was 5 GPa, and a 10 Hz sine wave was used.

4 Results and discussion

Figure 4 shows the modulated EXAFS in k space and R space. The k range for Fourier transform is 2.5 to 10 Å^{-1}. In order to compare easily, the conventional static EXAFS at 5 GPa is shown in the dashed blue line at the top of Fig. 4. The conventional EXAFS equation can be expressed in the following simple form:

$$\chi = \sum_j A_j(k)\sin(kS_j + \Phi_j(k)). \qquad (3)$$

Comparing the Eq. (1) with (3), it can be found easily that the modulated EXAFS has a 90° phase shift and k weight more than the conventional static EXAFS. For convenience of comparison, we use the k weight in the former and k^2 weight in the latter. The phase shift is apparent in the figure. In addition, the amplitude of modulated EXAFS vibrations is proportional to the atomic distance change of each shell that is likely to be obtained by fitting the experimental data. The magnitude of the modulated signals is about three orders of magnitude smaller than that of the static EXAFS spectrum, as shown in Fig. 4. So generally, it is difficult to detect such weak signals by the traditional method. These observations are in accordance with the theoretical analysis.

ZnSe maintains a four-coordinated zinc-blende structure until 13.5 GPa and its structure has been well known from X-ray diffraction experiments [9], which can provide the suitable references for our experimental results. The first shell of Zn-Se was filtered by the inverse Fourier transform, and then

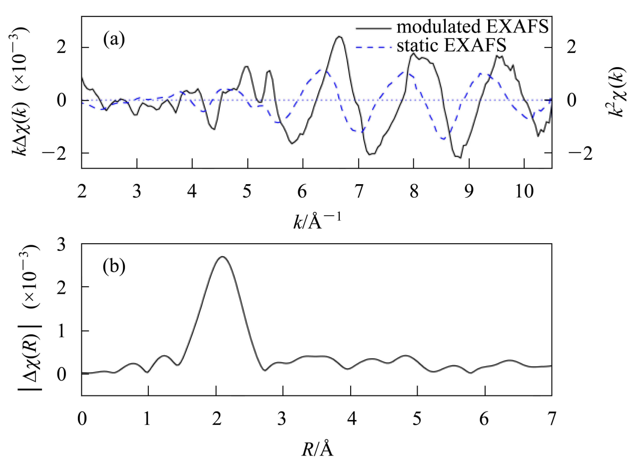

Fig. 4. Modulated EXAFS function has been shown in (a) k space and (b) R space.

fitted with Eq. (1). The fitting result is shown in Fig. 5. The mean atomic displacement of the first shell is 0.12±0.01 pm. Therefore, the value of $\Delta R/\Delta P$ for the first shell is 0.01 Å/GPa at 5 GPa, which is in good agreement with the Birch-Murnaghan state equation of ZnSe (as shown in Ref. [10]). All the results indicate the viability of the technique.

Pressure-modulated EXAFS is more sensitive to the change of local structure in a sample than conventional EXAFS techniques. At present we have got an accuracy of about 0.1 pm to atomic displacements. It is sure to achieve a higher resolution, even to a femtometer scale, by using an advanced synchrotron radiation source and perforated diamond anvils to reduce the absorption of X-rays [11], and so on. Meanwhile, with the help of dDAC, we can control the speed and magnitude of the response caused by the modulation of high pressure. Therefore it is convenient to study in situ the kinetics of phase transition.

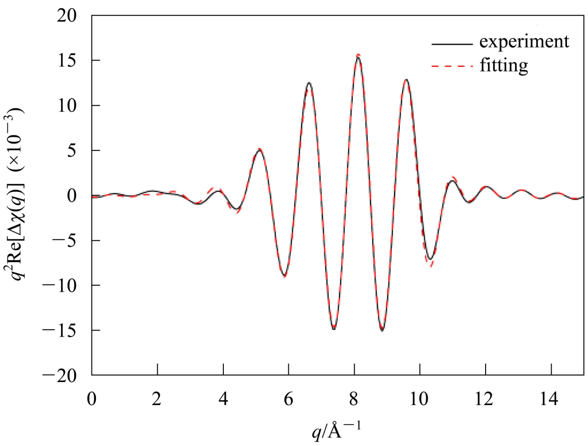

Fig. 5. The fitting results of the first shell between the experimental data and Eq. (1).

5 Conclusion

We have developed a pressure-modulated EXAFS method to perform higher resolution EXAFS measurements under the modulation of high pressure. EXAFS has become an important local structural tool in high pressure physics, especially for the study of noncrystalline materials. The development of our technique may provide a more sensitive tool to probe the small changes in the local scale caused by high pressure. Moreover, with the precise control of pressure by dDAC, it is possible to investigate the kinetics of phase transition in detail.

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