

# A new technique to measure the differential XAFS spectrum<sup>\*</sup>

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**Abstract:** A new technique has been developed for direct measurement of the differential X-ray absorption fine structure (XAFS) spectrum by the energy-modulation method. To acquire the energy-oscillating incident X-ray beam, a piezoelectric actuator is used to control the double-crystal monochromator. A logarithmic converter circuit and a lock-in amplifier are used to extract the modulated signals. The normal and differential XAFS spectra of the Mn K-edge of  $\text{Li}_2\text{MnO}_3$  have been collected. The X-ray-absorption near-edge-structure (XANES) spectra verify that the signal-to-noise ratio has been greatly improved by the new technique, and the extended X-ray absorption fine structure (EXAFS) spectra demonstrate that this new technique can efficiently enhance the signals of the backscattering atoms.

**Keywords:** differential XAFS, energy modulation, monochromator

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## 1 Introduction

X-ray absorption fine structure (XAFS) spectroscopy is a powerful tool to detect local atomic structure and electronic structure. Because the XAFS technique can be used for the measurements of local atomic structures of materials without long range order, such as glass, liquid and solutions, it has been widely used in physics, chemistry, material science, environmental science and so on [1, 2]. However, normal XAFS signals can easily be smeared by thermal or structural disorders, so small changes of the local atomic structure are difficult to distinguish. Therefore, developing a new XAFS technique to enhance the signal of local atomic structure is a widely interesting issue. A few decades ago [3–5], the modulation technique was confirmed to be a powerful tool to detect small changes of visible light reflection or absorption. Recently, it has been applied in XAFS experiments [6–10]. A periodic external perturbation, such as light [6], magnetic field [7], temperature [8], or high pressure [9, 10], has been verified to enhance the XAFS signal of internal structure. In 2001, an energy-modulation technique [11] for XAFS spectroscopy was first developed where another monochromator together with a piezo-driven oscillation stage were added to the beamline and used to modulate the energy. The result demonstrated that the energy-derivative X-ray absorption spectrum obtained indeed had higher energy reso-

lution and lower noise than the normal XAFS measurement. But in their report, only the differential spectrum in the XANES region was obtained. Evidently, further improvement of the energy-modulation XAFS technique is necessary.

In this study, a new energy-modulation technique has been developed and used to acquire the differential XAFS spectra. Without complicated changes to the beamline, the original double-crystal monochromator was improved to modulate the X-ray energy at given frequency. Combined with a logarithmic converter circuit (LCC) and a lock-in amplifier (LIA), the differential spectrum is expected to be successfully measured in both XANES and EXAFS regions. This newly-developed differential XAFS technique has been applied to the measurements of  $\text{Li}_2\text{MnO}_3$  and Nb samples. A detailed description of this new XAFS technique and its applications are discussed in this paper.

## 2 Theory

In the transmission mode of XAFS measurement, the XAFS spectrum can be obtained by collecting the X-ray intensities before and after sample absorption. When the incident X-ray energy ( $E$ ) is modulated by a small periodic fluctuation ( $\Delta E \cos \omega t$ ), the modulated absorption coefficient  $\mu(E + \Delta E \cos \omega t)$  can be expanded with a Taylor series as written in Eq. (1).

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$$\begin{aligned} \mu(E + \Delta E \cos \omega t) &= \mu(E) + \mu'(E) \Delta E \cos \omega t \\ &+ \frac{1}{2} \mu''(E) \Delta E^2 \cos^2 \omega t + \dots \end{aligned} \quad (1)$$

In Eq. (1),  $\Delta E$  is only a small energy change and  $\Delta E \ll E$ . By neglecting the higher-order terms, Eq. (1) can be expressed as Eq. (2):

$$\mu(E + \Delta E \cos \omega t) \approx \mu(E) + \mu'(E) \Delta E \cos \omega t. \quad (2)$$

From Eq. (2), It can be seen that the modulated XAFS spectrum contains a normal XAFS term  $\mu(E)$  and an amplitude-changeable differential XAFS term  $\mu'(E) \Delta E \cos \omega t$ .

### 3 Experiments

To perform the differential XAFS measurement, the incident X-ray energy needs to be modulated periodically. In 2001 [11], Suzuki et al added a channel-cut Si(311) crystal as the second monochromator, which cuts some part of the energy spread of the X-ray beam from the first monochromator. A piezo-driven oscillation stage was used to control the oscillation of the second Si (311) monochromator, so the central energy of the emergent beam changed periodically with the oscillation frequency of the second monochromator. This energy-modulated method needs a complicated alteration of the beamline by adding another monochromator. Especially, such a complicated project raises obvious difficulties to control the two monochromators synchronously. To realize the energy-modulation conveniently, a simpler strategy was adopted in our scheme to measure the differential XAFS spectrum. Instead of rebuilding the beam line, we only improved the double-crystal monochromator by adding a small piezoelectric actuator (PZT) fixed on the second crystal of the monochromator. This PZT was used to control the slight change of the parallelism between the two crystals of the double-crystal monochromator. According to Bragg's law, the central energy of the X-ray beam emerging from the monochromator is approximately linear with the interfacial angle between the two crystals if the interfacial angle is quite small. Therefore, the energy of the X-ray beam can be easily modulated by controlling the displacement of the PZT.

The displacement range of the PZT we used was 0–15  $\mu\text{m}$  with a precision of 0.3 nm. The initial position of the PZT was set to 2.1  $\mu\text{m}$ , which ensures a tight touch with the second crystal. To verify the linear relation between the PZT position and the emergent X-ray energy, the absorption coefficient of a Zr foil was measured in a small energy region around 18008.4 eV. It is known that the absorption coefficient of the Zr foil in such a small energy region is approximately linear with the incident X-ray energy as shown in Fig. 1(a). Therefore, the alteration

of PZT position causes the change of the absorption coefficient. Conversely, the central energy of the emerging X-ray beam can be calculated from the measured absorption coefficient of the Zr foil. A periodic position change of the PZT was applied to the second crystal of the monochromator, the absorption-coefficient change of the Zr foil was recorded and the emergent X-ray beam energy was further calculated. Figure 1(b) demonstrates that the position change of the PZT has the same tendency as the energy change of the emerging X-ray beam. The energy increased from 18008.2 to 18008.6 eV when the PZT extended by 0.9  $\mu\text{m}$ . This result illustrates that there is indeed a linear relation between the PZT position and the modulated X-ray energy.

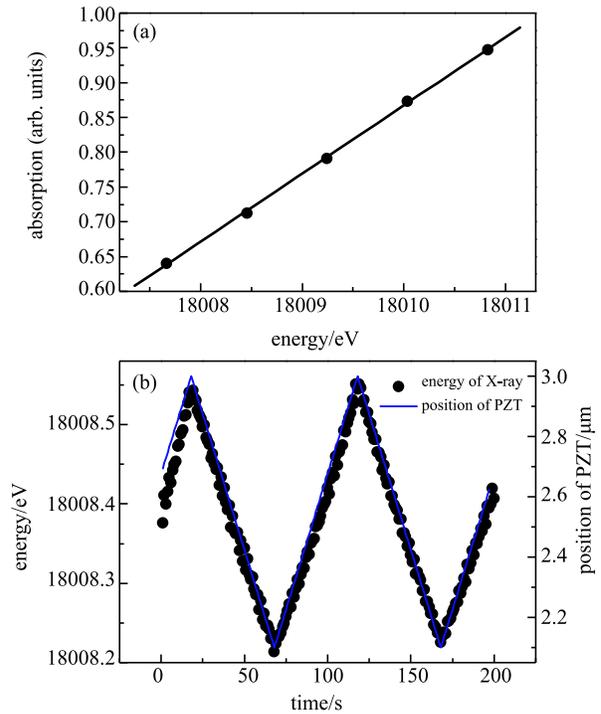


Fig. 1. (colour online) (a) Linear dependency of the absorption coefficient  $\mu$  of Zr foil on the incident X-ray energy  $E$  in a narrow energy region around 18008.4 eV. (b) The calculated X-ray energy from the X-ray absorption coefficient  $\mu$  of Zr foil (Black dots) and the two-periodic position change of the PZT (Solid line) on which a periodic ramp wave with frequency of 0.1 Hz was applied.

A schematic map of the differential XAFS measurement is shown in Fig. 2. A sine wave signal at a certain frequency was generated by the PZT driver and used to control the motion of the PZT in the monochromator. At the same time, a LIA was used as the reference signal. The emerging X-ray beam from the monochromator was energy-modulated by the periodic motion of the PZT, which resulted simultaneously in the variation of the absorption coefficient of the sample. A LCC was

used to yield a voltage signal corresponding to the absorption coefficient  $\ln(I_0/I)$ . To avoid the influence of intensity fluctuations, the LCC was designed to finish the transfers of each pair of the incoming ( $I_0$ ) and the transmitted ( $I$ ) intensities in less than 10  $\mu$ s. Finally, the LIA was used to extract the differential XAFS spectrum from the energy-modulated absorption signals. An LIA can detect and measure very weak periodic signals obscured by noise. A reference periodic signal with the same frequency as the measured signal is required to demodulate the input signal. Because of its good ability to suppress noise, LIAs have been widely applied in modulation techniques [12, 13].

All the experiments were performed at the XAFS stations of beamline 1W1B at Beijing Synchrotron Radiation Facility (BSRF), China.  $\text{Li}_2\text{MnO}_3$  powder and Nb foil were used as the samples and the differential XAFS data were collected at the Mn and Nb K-edges in the transmission mode. The energy step used in the XANES region was 0.3 eV for Mn and 1.0 eV for Nb. In the EXAFS region of Nb, the energy step was 2.0 eV. A voltage sine wave with frequency of 133 Hz was applied to the PZT driver for the Mn K-edge measurement with voltage magnitude of 4 V or for the Nb K-edge measurement with voltage magnitude of 2 V, which corresponded to an energy-modulation amplitude of 0.1 eV in the Mn K-edge measurement or 0.6 eV in the Nb K-edge measurement, respectively. The output of the LIA with a time constant of 1 s was transformed to high frequency signal and was cumulated to 5 s. For comparison, the same monochromator without PZT oscillation was also used to collect the normal XAFS spectrum.

## 4 Results and discussion

$\text{Li}_2\text{MnO}_3$  was chosen as the test sample because its XANES spectrum has many subtle fine structures. Figure 3 compares the Mn K-edge XANES spectra of  $\text{Li}_2\text{MnO}_3$ . A normal XANES spectrum is shown in Fig. 3(a). The energy-modulated XANES spectrum is shown in Fig. 3(b) (upper curve). The differential XANES spectrum obtained from the normal XANES spectrum (Fig. 3(a)) by a numerical differential is also shown in Fig. 3(b) (under curve). By comparison, it can be found that the energy-modulated XANES spectrum is in good agreement with the numerical differential XANES spectrum after normalization. We also note that the energy-modulated XANES spectrum removes some small and unwelcome glitches that are present in the numerical differential XANES spectrum. These glitches were from the noise and amplified by the numerical differential calculation. This result demonstrates that the energy-modulated XAFS technique can not only acquire the differential XANES spectrum but can also suppress the

unwelcome noise, increasing the signal-to-noise ratio.

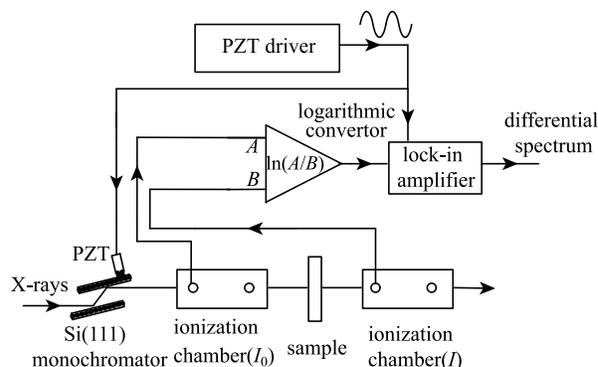


Fig. 2. Schematic map of the differential XAFS measurements. The PZT driver generated a sine wave signal as the input signals to the PZT in monochromator and the Lock-in Amplifier. The modulated absorption signals are extracted by the Lock-in Amplifier.

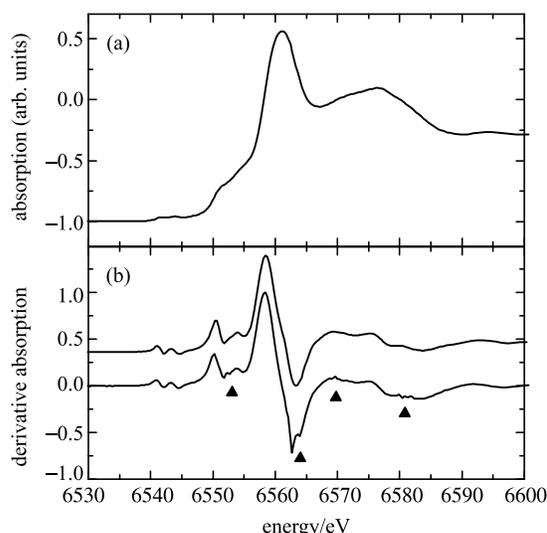


Fig. 3. (a) Normal XNEAS spectrum of  $\text{Li}_2\text{MnO}_3$  measured at the Mn K-edge. (b) Differential XNEAS spectrum of the same sample collected by using the energy-modulation technique (upper) and the differential XANES spectrum obtained by the numerical differential for the normal XNEAS spectrum (under). The small glitches from the noise were marked by black triangles, which were amplified by the numerical differential calculation.

Quadrupole transitions from Mn  $1s$  to the crystal field-split  $3d$  states will present a double-peak feature in the pre-edge region of the Mn K-edge XANES spectrum[14]. However, such a double-peak feature is hardly visible in the normal XANES spectrum as shown in Fig. 3(a), but it can be clearly observed in the energy-modulation XANES spectrum as shown in Fig. 3(b). The transition energy can be determined more precisely

from the center of the two peaks. This result demonstrates that the energy-modulated XANES technique can enhance the structural information, which enables the energy-modulation technique to be widely applied to the study of weak structural changes caused by external conditions.

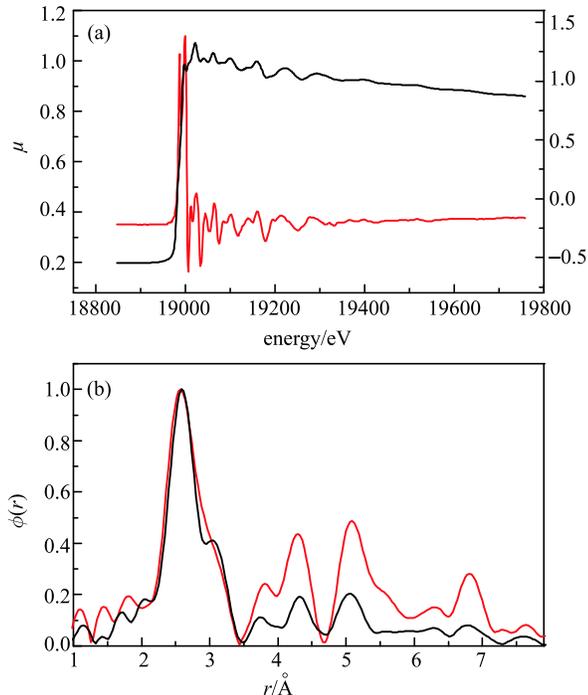


Fig. 4. (colour online) (a) Comparison of the normal (upper) and the energy-modulated (under) Nb K-edge X-ray absorption spectra of the Nb foil. (b) Comparison of the normal (under) and the energy-modulated (upper) Nb K-edge Fourier transform spectra of the Nb foil. The heights of the first coordination peaks have been normalized to 1.

Although the above study shows only the energy-modulated XANES spectra, this energy-modulated method is also easy to extend to the EXAFS region. Figure 4(a) shows a differential X-ray absorption spectrum of Nb foil from 18847 to 19758 eV. A normal X-ray absorption spectrum of this Nb foil is also compared in Fig. 4(a). It can be found that the differential X-ray absorption spectrum has more obvious oscillation structure but without an obvious edge-jump at the absorption edge. The energy-modulated EXAFS signal  $\chi_{\text{mod}}(E)$  can be extracted by a similar process to that in normal EXAFS. A Fourier transform (FT) analysis as formulated in Eq. (3) of EXAFS spectrum is important to obtain structure information [15]:

$$\varphi(r) = \text{FT}[\chi(k)], \quad (3)$$

where,  $\varphi(r)$  is the radial structure function of the absorbing atom,  $r$  is the distance from the absorbing atom to

the coordination shell, and  $k$  is the photoelectron wave vector, which is dependent on the incident X-ray energy  $E$  as listed in Eq. (4).

$$k = 2\pi/\lambda = \sqrt{2m(E - E_0)}/\hbar. \quad (4)$$

Here,  $m$  is the electron mass,  $\hbar$  is Planck's constant, and  $E_0$  is the energy threshold of the absorption edge. The modulated EXAFS spectrum can be expressed as Eq. (5):

$$\chi_{\text{mod}}(k) = \frac{d\chi(E)}{dE} = \frac{d\chi(E)}{dk} \cdot \frac{dk}{dE} = \chi'(k) \cdot \frac{2m}{\hbar^2 k}, \quad (5)$$

where,  $\chi'(k)$  is the primary derivative of  $\chi(k)$ . According to the known properties of the Fourier transform, the following relation formulated as Eq. (6) is tenable.

$$\text{FT}[\chi'(k)] = ir \cdot \text{FT}[\chi(k)]. \quad (6)$$

In Eq. (6),  $i$  is the imaginary unit. This formula tells clearly us that the signal from higher coordination shells with larger  $r$  will be enhanced in the differential EXAFS spectrum. The FT spectra of the normal and the differential EXAFS functions are compared in Fig. 4(b). Obviously, the structural signals from the higher coordination shells are significantly amplified in the FT spectrum of the differential EXAFS function. This result illustrates that the energy-modulated XAFS technique is beneficial to the study of weak high coordination shells. Although this energy-modulated XAFS technique has its obvious advantage in the measurements of some weak structures, the intensity decrease of the incident X-ray beam is noteworthy due to the detuning of the double-crystal monochromator caused by the energy-modulation. Although a LCC has been used to compensate the intensity fluctuation, there is still some influence of X-ray intensity change. Further improvements of the newly-developed energy-modulated XAFS technique are under study.

## 5 Conclusion

A new energy-modulation XAFS technique has been developed at BSRF. This newly-developed XAFS technique can be used to acquire the differential XANES and EXAFS spectra in the hard X-ray region. It is important that this energy-modulation technique is easy to implement with only a small alteration of the original double-crystal monochromator. The normal and energy-modulated XAFS measurements can be easily switched without any adverse influence. The differential XANES measurement can get higher signal-to-noise ratio and better energy resolution. The differential EXAFS measurement can enhance the weak structural signals. Due

to its sensitivity to subtle fine structures, this energy-modulated XAFS technique has potential applications in the measurements of subtle structural changes induced by external conditions, such as high temperature, low

temperature, high pressure and so on.

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