

# Total electron yield mode for XANES measurements in the energy region of 2.1–6.0 keV<sup>\*</sup>

ZHENG Lei(郑雷) ZHAO Yi-Dong(赵屹东) TANG Kun(唐坤)

MA Chen-Yan(马陈燕) HAN Yong(韩勇) CUI Ming-Qi(崔明启)<sup>1)</sup>

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

**Abstract:** The total electron yield (TEY) mode has been developed successfully for XANES measurements at Beamline 4B7A of BSRF (Beijing Synchrotron Radiation Facility). Its performance was studied by measuring sulphur K-edge XANES of three CdS samples (mixed with graphite powder as an electric conductor) with different concentration: 75%, 50% and 25%. The data are collected in TEY mode and fluorescence yield (FY) mode respectively for comparison. The results demonstrate that the TEY spectra of three samples agree well with each other after the background is subtracted and normalized. The measured XANES spectra by TEY mode without bias and with 100V bias are almost identical to one another, but the signal-to-noise ratio of spectra measured without bias is better than that with 100V bias. The consistency of the self-absorption corrected FY spectra and TEY spectra are within 10% for the three samples.

**Key words:** X-ray absorption near edge structure (XANES) spectroscopy, total electron yield (TEY), fluorescence yield (FY), 4B7A

**PACS:** 61.05.Cj, 78.70.Dm, 78.70.En **DOI:** 10.1088/1674-1137/35/2/018

## 1 Introduction

X-ray absorption near edge structure (XANES) spectroscopy is a widely used tool to elucidate local coordination environment and chemistry of the absorbing atom [1–4]. XANES is the region of an X-ray absorption spectrum within  $\sim 50$  eV of the absorption edge. The typical XANES experiment involves varying the energy of the incident X-ray beam through a suitable range of values encompassing the absorption edge of the element being investigated. So, data collection techniques are similar to those employed in the measurement of the X-ray absorption coefficient  $\mu(E)$ . Usually there are three measurements modes available, i.e. transmission, fluorescence yield (FY), and total electron yield (TEY). The transmission measurement, which is generally used in the hard X-ray region, would require very thin and free-standing samples in the soft X-ray region in which the absorption is much stronger. Although FY and TEY are alternative data collection modes that measure  $\mu(E)$  indirectly, only the two measurements methods

are suitable in the soft X-ray energy region of 2.1–6.0 keV. In using the FY mode, one must be mindful of the self-absorption effects [5] that become important for thick and concentrated samples. Because these corrections are difficult to apply a priori, the FY approach to data collection is typically reserved for very thin films and for samples where the element of interest is present in dilute quantities. For concentrated or thick samples, or when surface sensitivity is required, the best approach is TEY.

XANES measurements in the soft X-ray region of 2.1–6.0 keV have been performed at Beamline 4B7A of BSRF (Beijing Synchrotron Radiation Facility) exclusively employing FY mode for three years. However we often encountered difficulties when we tried to collect reliable spectra for highly concentrated samples. Strong fluorescence signal will increase the dead time of the Si(Li) detector. Although we can try to dilute the samples, insert attenuator or increase the distance between samples and detector, we need spend much time on trying many times. In addition, in general, it can be difficult to guarantee the success of

---

Received 5 May 2010, Revised 13 June 2010

<sup>\*</sup> Supported by National Natural Science Foundation of China (10775150)

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

©2011 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

the self-absorption correction, particularly if the entire composition of the sample is not well known [6]. Recently we have redesigned the sample holder, and the XANES data can be collected in both TEY and FY modes respectively. In this paper, we describe the investigation on the newly added TEY mode and demonstrate the performance of it.

## 2 Experiment

All data reported here were collected using Beamline 4B7A at the Beijing Synchrotron Radiation Facility of the Institute of High Energy Physics, Chinese Academy of Science. The optical elements of this beamline consist of a Ni-coated single-crystal Si plane mirror, a Ni-coated single-crystal Si toroidal cylindrical mirror with bender, and a double-crystal fixed-exit monochromator (KOHZU, Japan). The Ni-coated plane mirror accepts 5 mrad (horizontal)  $\times$  0.43 mrad (vertical) synchrotron radiation from the light source of the bending magnet and deflects the radiation with an angle of 1.1 degree to the cylindrical mirror, which parallels the plane mirror and focuses the beam to a 2.0 mm(H)  $\times$  1.0 mm(V) spot at the sample position. The monochromator located downstream the cylindrical mirror is equipped with a pair of Si(111) crystals. Passing through a low-pressure Kr gas ion chamber, the monochromatic light irradiates the samples in a vacuum chamber. Because the first mirror does not reflect X-rays above 6.0 keV and the second order harmonic diffracted by Si (111) is not allowed, the data presented here are free from error caused by harmonic radiation. The energy range of Beamline 4B7A is from 2.1 keV to 6.0 keV and the energy resolution power ( $E/dE$ ) is better than 5000 at 3206 eV and 1800 at 5465 eV respectively. The photon energy is calibrated using  $\text{Na}_2\text{SO}_4$  as reference for which the peak position of the white line was assigned a value of 2482.4 eV. During the time of data collection, the storage ring current ranged between 400 and 600 mA, with electron energy of 1.89 GeV.

During data collection, the incident monochromatic light flux for normalization was monitored by the Kr gas low-pressure ion chamber located upstream of the experimental station. For TEY measurements, the current from the ion chamber and sample were measured by a Model 485 picoammeter (Keithley, USA) and a Model 6517 A electrometer (Keithley, USA) respectively. For FY measurements, the current from the ion chamber was connected to a Model 428 current amplifier (Keithley, USA), which was fed through a V/F converter to a Keithley model

KPCI-3140 counter board. The fluorescence count of the element of interest in the sample was collected using a Si(Li) detector (PGT, USA) positioned perpendicular to the specimen surface. The counting data were recorded using different time ranging from two to five seconds per energy point for a full spectrum. A personal computer controlled the energy scans of the monochromator and had a real-time data acquisition from all needed instruments using our software programmed with LabVIEW®. The total time for each scan was approximately 12 minutes for TEY measurement and 18 minutes for FY measurement. The range for each scan was from 2440 eV to 2550 eV.

The schematic drawing of TEY mode for XANES measurement is shown in Fig. 1. The sample holder made of stainless steel is insulated from the metallic support using Teflon. The powder sample is pressed into a  $\phi 10$  mm pellet under a pressure of 12 MPa, and then the pellet is pasted on the sample holder using conductive double-sided carbon adhesive tape. Mixed with a certain amount of graphite powder, an insulating sample can be changed to be highly conductive. The sample holder is electrically connected to the ground through an electrometer, which also supplies the bias for the anode plate. In using TEY, one measures a sample current by biasing the sample relative to the anode plate and the ion chamber current is recorded for monitoring X-ray flux. The monochromatic X-ray impinges on the sample surface with an incidence angle of 45 degrees. A solid Si(Li) detector detecting the X-ray fluorescence emitted from the sample is positioned perpendicular to the incidence light and about 45 degrees relative to the sample surface. In order to reduce the intense absorption of air, the anode plate, sample, sample holder, fluorescence detector and parts of the circuit are mounted in a vacuum chamber, as shown in the dashed frame of Fig. 1.

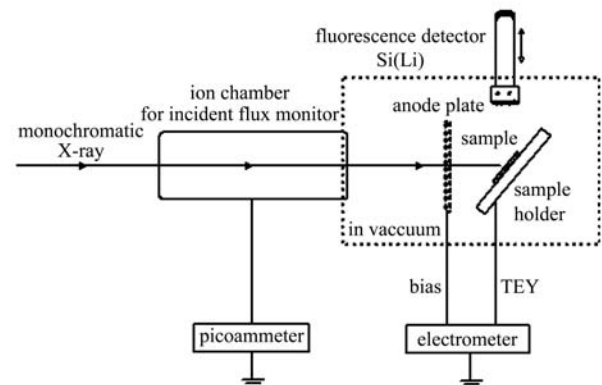


Fig. 1. Schematic drawing of TEY mode for XANES measurement.

In the present experiment, the material for sample preparation was cadmium sulfide (98%, Beijing Zhonglian Reagent Fine Chemicals Co., Ltd, China) mixed with graphite powder (98%, Tianjin Guangfu Fine Chemical Research Institute, China) for conduction. Three CdS samples were prepared at mass percentages of 75%, 50% and 25% respectively. Background subtraction and normalization of XANES data of all three samples were performed with the package ATHENA [6].

### 3 Results and discussion

Figure 2 shows S K-edge XANES spectra of 75%, 50% and 25% CdS samples measured by the TEY mode with 0 V bias. As clearly shown, the three XANES spectra are nearly identical to one another, except that there is somewhat discrepancy at photon energy point of 2482.4 eV. The data of sample current versus bias have been measured at two energy points, which are chosen below edge and above edge respectively. The obtained results indicate that the bias of 100 V will make the sample current at plateau. Fig. 3 shows the S K-edge XANES spectra of 75% CdS sample measured by TEY mode without bias and with 100 V bias together. As can be seen in Fig. 3, the two spectra are almost identical to each other. In addition, the spectrum measured with bias 100 V has a slightly lower signal-to-noise ratio than that measured without bias in the energy region above 2520 eV, shown in the inset of Fig. 3. It is concluded that the XANES spectrum is almost not affected by the magnitude of bias. As far as 50% and 25% CdS samples are concerned, they have the same conclusion as the 75% CdS sample.

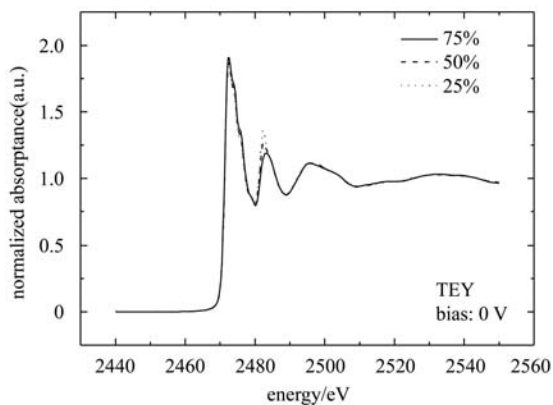


Fig. 2. Sulfur K-edge XANES spectra of 75%, 50% and 25% CdS measured by the TEY mode with 0 V bias. The solid line denotes 75% of the CdS sample; the dashed line denotes 50% of the CdS sample; the dotted line denotes 25% of the CdS sample.

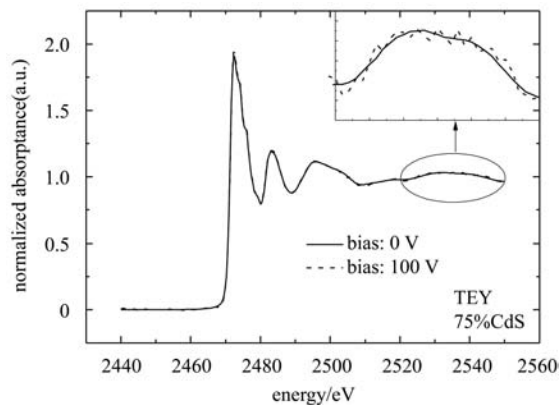


Fig. 3. Sulfur K-edge XANES spectra of 75% CdS measured by the TEY mode without bias and with 100 V bias. The solid line is without bias; the dashed line is with 100 V bias.

Figure 4 shows S K-edge XANES spectra of 75% CdS samples measured by the TEY mode without bias and FY mode. The self-absorption corrected FY spectrum is also shown in Fig. 4. The self-absorption correction was performed with the package ATHENA [6]. The intensity of the white line of the TEY spectrum is 1.90, while the intensity of the FY spectrum is only 1.55. Significant reduction of the FY spectrum is known to be due to the self-absorption effect, since there are considerable S atoms and light atoms of C in the 75% CdS sample. After the self-absorption is corrected, the intensity of the white line of the FY spectrum is increased to 1.84, which is very close to the intensity of the TEY spectrum. In addition, the entire components of the majority of samples are not always known, in which case self-absorption correction can not be performed for the FY mode. So the

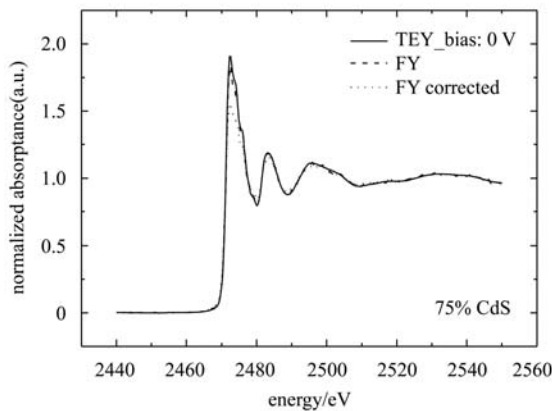


Fig. 4. Sulfur K-edge XANES spectra of 75% CdS measured by the TEY mode and FY mode. The solid line is for the TEY mode without bias; the dashed line is for the FY mode; the dotted line denotes the self-absorption corrected FY spectrum.

TEY mode is suitable for thick and concentrated conductive samples, for which the use of FY mode will result in unreliable XANES spectra.

## 4 Summary

We have developed the total electron yield (TEY) mode for XANES measurements at Beamline 4B7A of

BSRF (Beijing Synchrotron Radiation Facility). The samples with different concentration almost have the same XANES spectra measured by the TEY mode. The XANES spectra measured without bias are almost identical to those with bias. For thick and concentrated conductive samples, measurements by the TEY mode will give more reliable results compared with the FY mode.

---

## References

- 1 HU Y F, Sham T K, ZOU Z et al. *J. Synchrotron Rad.*, 2001, **8**: 860–862
- 2 Fleet M E, LIU Xiao-Yang, Harmer S L et al. *The Canadian Mineralogist*, 2005, **43**: 1605–1618
- 3 Farges F, Keppler H, Flank A M et al. *Journal of Physics: Conference Series*, 2009, **190**: 012177
- 4 Mijovilovich A, Pettersson L G M, Mangold S et al. *J. Phys. Chem. A*, 2009, **113**(2): 2750–2756
- 5 Pickering I J, Prince R C, Divers T et al. *FEBS Lett.*, 1998, **441**: 11–14
- 6 Ravel B, Newville M. *J. Synchrotron Rad.*, 2005, **12**: 537–541