

Beamline Practice at BL27SU

Soft X-ray photoabsorption spectroscopy using fluorescence yield method

Ver. 2011/09/09
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1. Introduction

The beamline BL27SU is used for X-ray absorption applications in the soft X-ray region (0.17-2.8 keV). In this practical training course, the participants will learn how to measure soft X-ray absorption spectrum. The participants will gain experience in sample preparation, sample handling, and data acquisition. Soft X-ray absorption spectra will be measured by means of *the total electron yield* method, *the total fluorescence yield* method using a PIN photodiode detector and *the partial fluorescence yield* method using a silicon-drift-detector.

2. Practice plan

9:30~ Introduction

10:00~ Practical training-1 (Measurement of total electron and total fluorescence yield spectra)

12:00~ ----- Lunch -----

13:30~ Practical training-2 (Measurement of partial fluorescence yield spectra)

17:30 ----- Close -----

3. What is a soft X-ray photoabsorption spectroscopy?

X-ray photoabsorption spectroscopy (XAS) is a widely-used technique for determining the local geometric and/or electronic structure of matter [1,2]. Since the core electrons are localized around the atoms to which they originally belonged, XAS is an element-specific spectroscopic technique.

Because the XAS spectra are characterized by many fine features near the absorption edge, XAS is generally called X-ray absorption fine structure (XAFS) spectroscopy. The XAFS spectra are usually divided into two energy regions: the X-ray Absorption Near Edge Structure (XANES) and the extended X-ray absorption fine structure (EXAFS). XANES typically represents the energy region from the absorption edge to about 50 eV above the absorption edge. The absorption structures near the absorption edge were first interpreted by *Kossel* as due to electronic transitions to unoccupied molecular orbitals. The oscillatory structure extending for hundreds of electron volts past the edges is called EXAFS, and it was theoretically interpreted by *Kronig* to the single scattering of the excited photoelectron by neighboring atoms. The energy region of XANES (extending over a range of about 100 eV) between the edge region and the EXAFS region has been assigned to multiple scattering

resonances.

XAS in the soft X-ray region is a powerful tool for chemical state analysis of the low-Z elements, and it is often called NEXAFS (Near Edge X-ray Absorption Fine Structure) spectroscopy. NEXAFS is synonymous with XANES, but XANES is more commonly used for solids and inorganic compounds, while NEXAFS is used for organic compounds in the surface and molecular science. In the practical training course, the participants will experience how to measure XAS in the soft X-ray region.

4. How to obtain soft X-ray absorption spectrum?

XAS is the measurement of the x-ray absorption coefficient [$\mu(E)$] of a matter as a function of excitation energy. The most faithful method to obtain the absorption coefficient is a transmission method based on the *Beer-Lambert law*. When X-rays of a narrow band width are irradiated on the sample, the absorption coefficient ($\mu(E)$) can be determined from the following equation.

$$I_t = I_0 e^{(-\mu(E)x)} \quad (1)$$

Here, (I_t) is number of x-ray photons that are transmitted through a sample, (I_0) is the number of x-ray photons irradiated on the sample, and (x) is the thickness of the sample. However, the X-ray transmission method, which is ordinarily used in hard X-ray measurements, is not appropriate for the soft X-ray measurements, because the soft X-ray absorption coefficients are too large for practical sample thickness to use the transmission method. Therefore, to obtain the XAS data in the soft X-ray region, we have to detect another signal which is proportional to the soft X-ray absorption coefficient.

The soft X-ray absorption coefficient can be observed by measuring either the electron yield or the fluorescent yield. The fundamental phenomenon in soft X-ray absorption is an excitation or an ionization of a core electron. The resulting core hole is filled by an electron from another shell and followed by either an Auger electron or X-ray fluorescence emission. Both channels can be used as a probe of the probability of the creation of a core hole via soft X-ray absorption. Here, it should be noted that the spectra measured by electron yield and fluorescent yield methods are not identical to that obtained by the transmission method. In general, the electron yield is surface sensitive and the X-ray fluorescence yield is bulk sensitive. In other word, the surface or bulk sensitivity can be controlled by different yield methods, and we can obtain deeper information on the chemical and electronic states of matter from the XAS measurements. In the practical training course, the participants will learn the techniques for measuring the chemical states of matter by using the electron yield and the fluorescent method.

5. Experimental

5-1. Light source and optics of beamline BL27SU.

Figure 1 shows a layout of the BL27SU. The light source is a Figure-8 undulator which can produce linearly polarized radiation with low on-axis heat load [3]. Figure-8 undulator provides both horizontally and vertically polarized soft X-ray beams by choice of an appropriate undulator gap, the linear electric vector lying horizontally (0°) from the integer-order-harmonic light and that vertically (90°) from the half-integer-order light.

The monochromator is a varied-line-spacing plane grating (VLS-PGM) fixed deviation instrument of the Hettrick type [4]. The monochromator consists of the entrance slit (S1), spherical mirrors (M21, M22), three gratings (G1, G2, G3), and exit slit (S2). Two spherical mirrors and three gratings allow the scanning of an energy range from 170 to 2800 eV. Energy sweep can be done only by the rotation of the grating. Absorption spectra are measured by scanning the undulator gap as well as the monochromator to keep the maximum intensity of the incident soft x-rays. Three re-focusing mirrors are designed for focusing the photon beam on three experimental stations arranged in tandem.

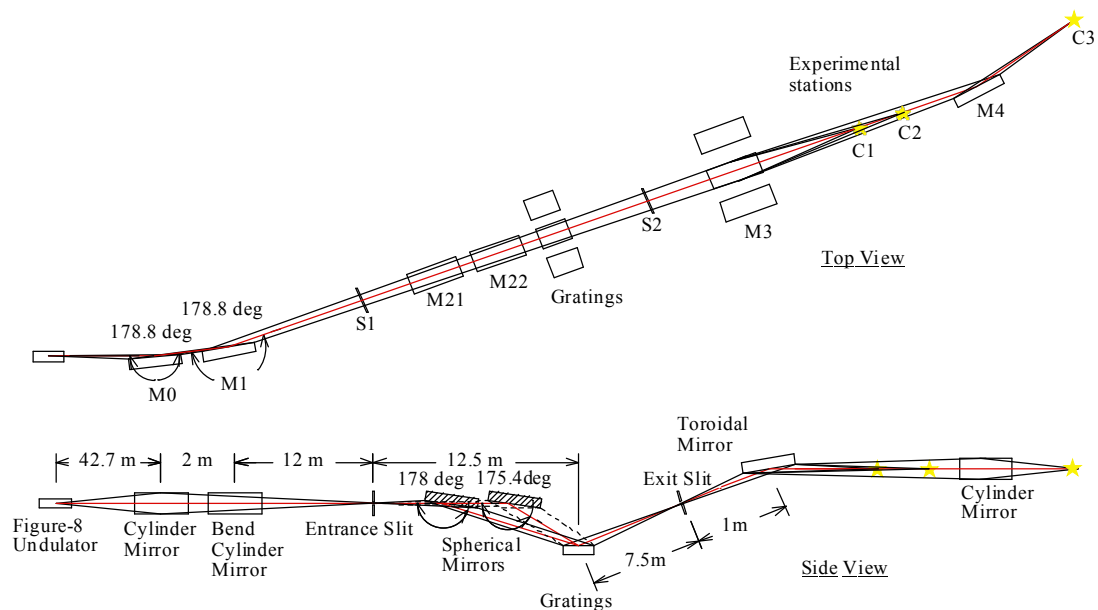


Figure.1; Layout of the BL27SU

<In the practice course, the alignment and the calibration of optics are omitted. The outlines of calibration procedures will be explained in the guidance. >

5-2. Sample handling

The standard procedure in soft X-ray experiments is to install all equipment necessary for experiments inside the high-vacuum chamber, since soft X-rays below 1.5 keV are fairly absorbed in atmospheric air. The high-vacuum chamber produces an ideally clean environment, therefore, it gives good opportunities to investigate a clean surface and anaerobic materials. On the other hand, the vacuum condition has drawbacks. Technologically significant phenomena take place under higher-pressure regions (1~760 mbar). One approach to overcoming the absorption in atmospheric air is to use a Helium-path instead of an air-path. Helium gas has a higher transmission than air in the soft X-ray region due to its smaller atomic number. In the BL27SU, a differential pumping system was developed for use with windowless soft X-ray experiments under normal atmospheric pressure helium conditions [5]. This technique can eliminate the loss of incident photons due to the absorption of vacuum windows.

Figure 3 shows the transmission curves of soft X-rays under atmospheric helium. The experimentally determined transmission curves are nearly identical to the simulated ones. The transmission at 550 eV (the oxygen K-edge region) measured at 10 mm downstream of the first aperture is about 85%. When the photon flight path in the atmospheric pressure region is expanded up to 50 mm, more than 70% of the incident photons are transmitted to the detector. Although the transmission is decreased in the lower photon energy region, about 60% of the incident photons are transmitted to the detector at 350 eV.

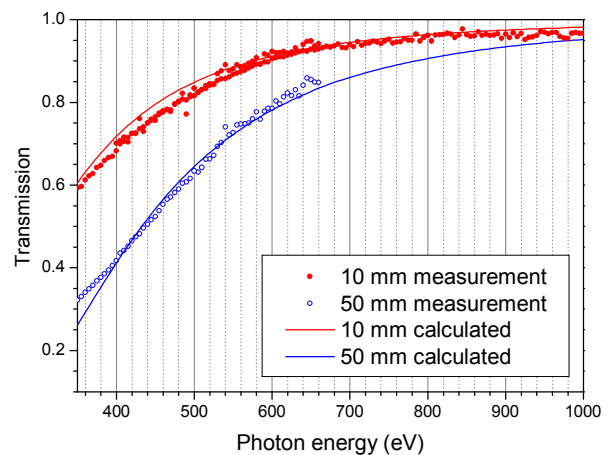


Figure 3: Experimental and calculated transmission curves of soft X-ray photons obtained under helium-path conditions. The experimental transmission curves were measured at the helium-path length of 10 mm (●) and 50 mm (○). The solid (10 mm) and dashed (50 mm) lines are the simulated transmission curves of the fabricated differential pumping system.

In the practical training course, the participants will gain experience in sample preparation, sample alignment inside a vacuum chamber. Additionally, the soft X-ray experiments under the atmospheric pressure condition are also experienced.

6. Electron and Fluorescence yield methods

6-1, Electron yield detection

Electron elimination processes can be classified into three types. First, *the photoelectrons* can originate from both core and valence electron ionization, if the incident photon energy is higher than the binding energies of these electronic states with respect to the vacuum level. Secondly, following a core electron excitation or ionization, an electron in a higher energy level falls into the core hole, and another electron is eliminated using a released excess energy. This second electron is called an *Auger electron*. The kinetic energy of photoelectron depends on the incident photon energy. On the other hand, in contrast to the photoelectron, the kinetic energy of Auger electrons is characteristic for specific Auger transition and is independent of the incident photon energy. The photoelectron or Auger electron emitted in the solid may hit a neighboring molecule, so that it induces an electron impact ionization of the neighboring molecule. Third are *secondary electrons* which are emitted by such an inelastic scattering processes with primary electrons.

In generally, the electron yield method is surface sensitive. The sensitivity to surface and bulk compositions is different among the above three electron detection, since the mean free path of electron strongly depends on the kinetic energy, and it is well known as *a universal curve* [1]. The surface sensitivity of each electron yield method is estimated by the mean free path of electrons. Further, while the secondary electron loses the memory of initial excitation site, the photoelectron and the Auger electron are remembering an initial excitation site, because these electrons are eliminated with a specific kinetic energy. Selective detection of such a specific energy electron improves the element selectivity in the XAS measurements.

6-2. Total electron yield method

The total electron yield (TEY) method measures the yield of all photoelectrons, Auger electrons, and secondary electrons. Due to the large mean free paths of the low energy electrons, the electron yield signal in TEY method is dominated by the low energy electrons with kinetic energies below 10 eV. One drawback of the electron yield detection is sensitive to sample charging. Therefore, the application to the insulator samples is restricted.

Figure2 illustrates the setup of the total electron detection. The detection of a sample current is the simplest method for XAS in the soft X-ray region, and is equivalent to the total electron yield (TEY) measurement. In this method, the sample is connected to ground through an ammeter and the neutralization current is monitored.

Alternatively, it is also possible to measure the electron yield spectrum by detecting the eliminated free electrons. In this case, a micro-channel-plate (MCP) detector is commonly used. The detection efficiency of the MCP to the electron is about 30%, so the detection efficiency of the electron lowers compared with the sample current method. On the other hand, the trajectory of the free electron can be controlled by electric and magnetic fields. By using the energy filter to the incoming free electron, it is possible to detect a specific energy electron.

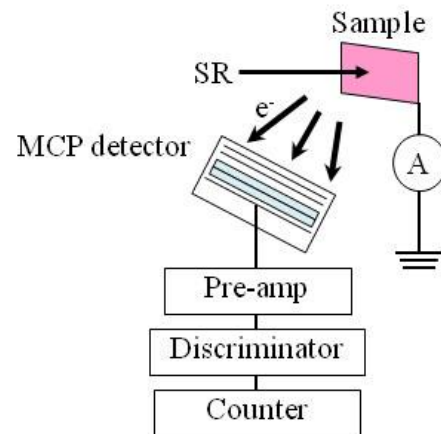


Figure 2; An examples of TEY measurement using sample current method and MCP detector.

6-3. *Partial electron yield (not scheduled in this practical course)*

The partial electron yield (PEY) method collects a fraction of the total electrons by using an electron energy analyzer. The simplest way to obtain the PEY signal is to placing a retarding electric field in front of the electron detector, it is called a high-path filter method. The typical bias voltage is in the order of ~ 100 eV, which rejects low energy electrons. The drawback of this method is that it detects both photoelectrons and Auger electrons, as long as their kinetic energies exceed the bias voltage. The PEY method also detects electrons that undergo inelastic collisions with the substrate atoms, as long as their final kinetic energies are higher than the retarding bias voltage. Therefore, the energy selectivity in retarding field method is restricted. Another PEY setup is to using a high resolution electron energy analyzer such as a cylindrical electron energy analyzer or a hemispherical electron energy analyzer. For example, the kinetic energy of Auger electrons is characteristic for specific Auger transition and is independent of the incident photon energy. The Auger electron yield (AEY) can be obtained by setting the energy analyzer at specific transition energy.

6-4, *Fluorescence yield detection*

The core hole created by soft X-ray absorption is accompanied by either the fluorescence decay or Auger decay. Although the fluorescence yield detection is the most common method in the hard X-ray energy regime, it is relatively difficult in the soft X-ray region. While the fluorescence decay is a dominant channel for the relaxation of K -shell hole at $Z > 30$, its contribution is much smaller than the Auger decay at $Z < 30$. For example, the relative fluorescent decay probability for the oxygen K -edge is less than 1% [1].

Although the yield is low, the fluorescence yield measurement has unique advantages over the electron yield method.

(1) The detection of fluorescence yield is insensitive to sample charging. It makes applicable to measure the XAS of insulating materials. This advantage is very important in the investigations of transition metal compounds and inorganic materials such as the glasses and ceramics.

(2) It has a much deeper detection limit than the electron yield method. Simultaneous collection of both fluorescence and electron yield provides an opportunity to distinguish the electronic properties between surface and bulk of materials.

(3) Fluorescence measurement is possible under the non-UHV conditions, allowing studies of reaction kinetics under in-situ conditions.

6-5. Total fluorescence yield

A fluorescence yield detector is mainly composed of PIN photodiode detector or microchannel-plate-detector (MCP). The PIN photodiode detector is possible to use under the non-UHV condition and the detection sensitivity is higher than the MCP detector. One drawback of the PIN photodiode is highly sensitive to the visible light. For example, the visible lights that eliminated by a filament of ion-gauge and enter from a viewing-port make higher background.

On the other hand, the pulse counting detection is possible by using MCP detector. By discriminating each pulse signal, the data of a high S/B ration can be obtained. Figure 3 shows the fluorescence yield analyzer using MCP. A negative high voltage is applied on the entrance of the MCPs to repel electrons. Further, a grid placed in front of the detector. The grid is used to prevent ions from coming into the MCPs. Then, the fluorescence can exclusively be detected by the MCPs.

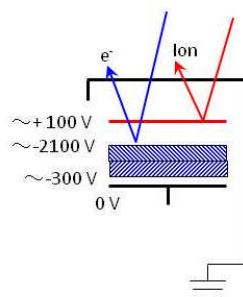


Figure 3; An example of the total fluorescence yield analyzer using MCP.

Practical training - 1

XAS of metallic sample will be measured by using the TEY and TFY method. TEY spectrum is obtained by sample current method, and the TFY spectrum is measured using PIN photodiode detector. Participants will be experienced that the XAS measurement distinguishes the electronic states of the oxidized surface and the bulk of metallic sample.

6-6. Partial fluorescence yield

One major drawback of total fluorescence yield detection is its low S/B ratio to the measurement of low concentration samples. The detection sensitivity of the total fluorescence yield method is approximately 1%. An alternative approach is partial fluorescence detection which is possible by using an energy-dispersive detector. The energy of fluorescence X-ray is characteristic for each element as well as Auger electron. Selective X-ray fluorescence detection can improve the detection sensitivity, and XANES spectra have been obtained for elements of concentrations lower than 100 ppm. For fluorescence measurements of concentrations above 0.1%, the total fluorescence detection is preferable, however, for lower concentrations the partial fluorescence yield detection is a better.

A silicon drift detector (SDD), which is a semi-conductor detector, is one of the widely applied detectors to XAFS measurement [6]. The principle of the SDD was first proposed by Gatti and Rehak [7], and is now commercially available. The SDD is unique because it achieves a higher energy resolution and higher count rate at shorter shaping times compared to conventional semi-conductor detectors, and it can be used near room temperature. The high count rate of the SDD can compensate for low fluorescence yield in the soft X-ray region, and it can distinguish the fluorescence line of interest from the peak caused by elastic scattering and from neighboring fluorescence lines.

The SDD used in the present practice was purchased from OURSTEX Corporation Ltd. (X Flash Detector, 1201 series). The active area of the photodetection element is 30 mm². The entrance window mounted on the front of the detector is a MOXTEK AP3.3 window consisting of ultra-thin polymer film (300 nm thick, density 1.4 g/cm³) and is supported by 38 μm thick rigid silicon grid with 77% open area. The SDD module equipped with the AP3.3 window provides an X-ray transmission to the detector as low as B K α X-ray energy (170 eV), i.e., our detector is applicable to the XANES experiment at a boron K-edge. The AP3.3 window is vacuum-tight, but is not "helium-tight". Therefore, it cannot be used in the helium path.

Practical training - 2

In the practical training-1, the participants will be experience that the detection limits of the TEY and the TFY method is ~1%. In the practical training-2, XAS is obtained by the PFY method with SDD detector. By selectively measuring the fluorescence signal from a specific element, it will be experienced that the detection sensitivity is drastically improved.

References

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