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The XAFS beamline of SSRF*

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The BL14W1 beamline at Shanghai Synchrotron Radiation Facility (SSRF) is an X-ray absorption fine-structure (XAFS) beamline, for investigating atomic local structure, which is demanded extensively in the fields of physics, chemistry, materials science, environmental science and so on. The beamline is based on a 38-pole wiggler with the maximum magnetic field of 1.2 T. X-rays of 4.5–40 keV can be extracted by the optical scheme consisting of white beam vertical collimating mirror, liquid-nitrogen-cooled double crystal monochromator of Si(111) and Si(311), toroidal focusing mirror and higher harmonics rejection mirror. The maximum photon flux about 5×10^{12} photons/s at the sample at 10 keV, with a beam size of 0.3 mm × 0.3 mm. The beamline is equipped with four types of detectors for experiments in either transmission or fluorescence mode. At present, quick-XAFS, grazing incidence XAFS, X-ray emission spectroscopy, high-pressure XAFS and time-resolved X-ray excited optical luminescence methods have been developed.

Keywords: Shanghai Synchrotron Radiation Facility, X-ray absorption fine structure, BL14W1

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I. INTRODUCTION

X-ray absorption fine structure (XAFS), being capable of obtaining local structure information, has become a technique on wide use in physics, chemistry, materials science, life science, environment studies, etc. [1]. Dedicated for general XAFS measurement, BL14W1 is one of the Phase I beamlines at Shanghai Synchrotron Radiation Facility (SSRF), a third generation light source with a 3.5 GeV storage ring [2] running 250 mA electron beam current in the top-up injection mode. Its construction was completed in December 2008 and has been opened to users since May 2009. The users, from universities and research institutions, and industries as well, have been performing their experiments in a variety of research fields. To date, BL14W1 has delivered in total 24 000 hours of beamtime to users of over 300 research groups. The outcome was appealing, of which 55 papers were published in top journals [3–11]. In this paper, we present a review on the facilities and experimental methods of the XAFS beamline.

II. THE BEAMLINE

A. The wiggler source

The X-ray source of BL14W1 is a 1.5-m long wiggler of 38 poles in a period of 80 mm, with the maximum magnetic field strength of 1.2 T, the critical energy of $E_c = 10$ keV and the wiggler deviation parameter of $K = 8.8$. With a total power of 5 kW, the wiggler source can emit approximately 1×10^{13} photons/s at 10 keV (Table 1). The flux at sample in focus mode is given in Fig. 1.

TABLE 1. Specifications of the BL14W1 beamline

Equipment	Specifications
Light source	38 pole wiggler
Electron energy (GeV)	3.5
Magnetic field intensity (T)	1.2
Beam intensity (mA)	250
Acceptance angle (mrad)	1.0 × 0.1 (H×V)
Energy range (keV)	4.5–20, Si(111) focused; 8–40, Si(311) unfocused
Energy resolution ($\Delta E/E$)	1.5×10^{-4} Si(111) @10 keV
Flux at sample (phs/s)	$> 5.0 \times 10^{12}$@10 keV Si(111) focused, 250 mA
Minimum spot size (mm)	0.3 × 0.3 (H×V)
High harmonic content[a]	$< 10^{-4}$
Detection mode	Transmission, fluorescence

[a] Harmonic suppression mirror (focused)

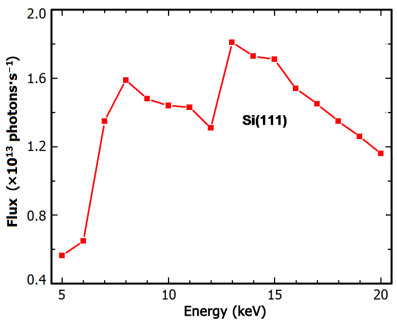

Fig. 1. (Color online) Flux at sample in Si(111) focus mode.

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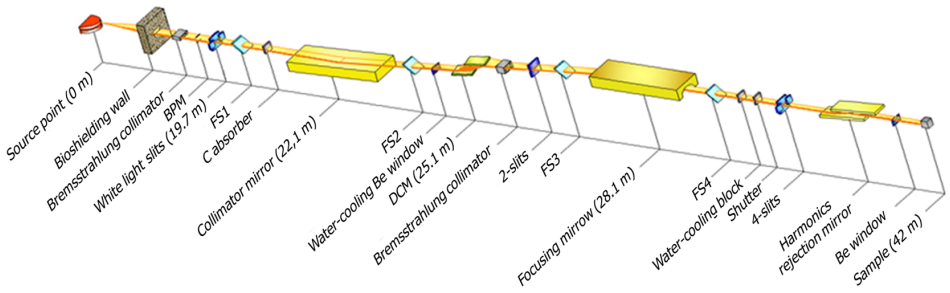

Fig. 2. (Color online) Schematic diagram of BL14W1 in focus mode.

B. Beamline optics

The layout of BL14W1 beamline is shown schematically in Fig. 2. It consists of a front end, a collimating mirror, a double-crystal monochromator (DCM), a focusing mirror, a harmonics rejection mirror and the end-station.

The first mirror (placed at 22.1 m from the source point) provides vertical collimation. Made of silicon, and coated with 500 Å thick rhodium (Rh), it has an optically active area of 1000 mm (l) × 40 mm (w). The mirror surface is polished to an RMS roughness of < 3 Å, with sagittal slope errors of < 2 μrad. Having a side-water cooling, the mirror is operated under ultra-high vacuum (UHV) conditions. It is set at a grazing incident angle of 2.8 mrad, and reflects light upward.

The DCM, from ACCEL Instruments GmbH, is positioned at 25.1 m from the source point. Cooled with liquid nitrogen, its crystal pair can be precisely positioned and oriented in the X-ray beam to provide mono-energetic photon beams of 4–50 keV, by using interchangeable pairs of Si(111) and Si(311) crystals, in either focusing or non-focusing mode.

The toroidal mirror is placed at 28.1 m away from the source and focuses the beam to the sample position at 42 m with both horizontal and vertical directions. It has an optically active area of 1000 mm (l) × 40 mm (w).

Just before the sample chamber, a harmonics rejection mirror is used to restrain higher harmonics to less than 0.1%. It has three coating layers of silicon, nickel and rhodium, and is set at a grazing incident angle of 5 mrad.

Currently, BL14W1 is operated in two modes: 1) focusing mode, in which the X-ray goes through collimator mirror, LN DCM, focusing mirror, and harmonics rejection mirror to reach to the sample position with a spot size of < 0.3 mm × 0.3 mm; 2) unfocused mode, in which the X-ray goes through only LN DCM to reach the sample position, with a maximum spot size of 40 mm × 4 mm, tuned by the end-station slits. An operational mode is switched to another mode, normally during beamtime, within one hour.

C. Experimental stations

Figure 3 shows schematically the XAFS experimental station of BL14W1. It is based on a 1.2 m × 2.4 m optical table with a load design of 300 kg. It is equipped for standard XAFS measurements, including multi-dimension sample stage, three ionization chambers, a Lytle detector (The EXAFS Co.), a multi-element (32) Ge solid-state detector (SSD, Canberra, USA), and a 4-element silicon drift detector (SDD, X-Flash 5040, Bruker, Germany).

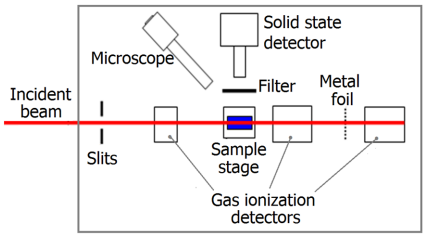

Fig. 3. (Color online) Schematic diagram of the experimental station at BL14W1.

The sample stage, computer-controlled, performs vertical and horizontal translations within micrometer precision. A goniometer tilts the sample (±5°) along the X-ray beam, while another goniometer rotates the sample (360°). The sample holder can be used in transmission or fluorescence yield modes, and the best sample size is no less than 5 mm. A multi-sample holder will be designed to improve efficiency of the user experiments.

Standard XAFS measurements are performed in transmission or fluorescence yield modes. In transmission XAFS, three ionization chambers are used. An automatic gas distribution system with He, N_2, Ar and Kr is connected to the ion chambers for optimum absorption at different energies. In fluorescence yield XAFS, three types of detectors can be used for different elemental concentrations. For elemental concentrations above of 1000 ppm, the large solid angle Lytle detector is preferable, while for low elemental concentrations, the 4-element SDD or the multi-element Ge SSD is a better option. The 4-element SDD (Bruker X-Flash 5040) is a 40 mm^2 silicon drift detector with an energy resolution of < 123 eV (Mn K_α) at 1 Mcps, accepting maximum input count rates in excess of 3 Mcps. The multi-element (32) Ge SSD (Camberra, USA) has higher efficiency and lower detection limit than those of the 4-element SDD, though it must be cooled by liquid nitrogen in order to reduce the thermal generation of charge carriers (thus reverse leakage current) to an acceptable level.

D. Control and data-acquisition system

The control and data-acquisition in BL14W1 XAFS station is performed by EPICS (Experimental Physics and Industrial Control System) and LabVIEW software. The two systems are communicated by using NI (National Instrument) LabVIEW's Data logging and Supervisory Control (DSC) module. To our knowledge, BL14W1 is the first XAFS station to use such method. The EPICS system is common for all beamlines in SSRF to control motors. EPICS provides a standard distributed control system architecture, communication protocol, run-time database and software tools, and supports many I/O devices.

Data acquisition software is compiled by LabVIEW, which is advantageous in its user-friendly graphical interface with its easy control model for different types of hardware. It is divided into the ordinary scan mode and detector scan mode, which can be chosen according to the sample concentration. In the future, we will switch the LabVIEW system to EPICS system, which provides more drivers to support various devices and its user interface is much friendlier. Then, efficiency and reliability of the control and data-acquisition system, of EPICS, can be improved significantly.

III. EXPERIMENTS METHODS

In addition to standard XAFS measurement, quick-scanning XAFS method (QXFAS), X-ray emission spectroscopy (XES), grazing incidence XAFS (GIXAFS), high pressure XAFS, and time-resolved X-ray excited optical luminescence (TR-XEOL) have been developed.

A. Quick scanning XAFS method

Time-resolved technique is important for investigating dynamic structural changes of physical processes or chemical reactions. So, the QXAFS method based on EPICS and LabVIEW was developed at BL14W1 [12]. Figure 4 shows schematically the QXAFS system. As the monochromator working at constant speed, the ADC with 1 MHz sampling rate is used to acquire signals from three iron chambers, while one scaler is used to calculate the scanning energy precisely by recording the number of monochromator control pulses. The two cards are synchronized by an external hardware trigger. Analog-to-digital converter and double-crystal monochromator setup are utilized to optimize the QXAFS parameters. The alignment is solved using a standard sample placed between the second and third ionization chambers. The standard sample spectra can be used to align in the same energy position. A good QXAFS spectrum with an energy range of 1.2 keV at the Cu K-edge can be collected in 2 s with stable beam position. The obtained data quality is comparable to those collected under the step mode (Fig. 5).

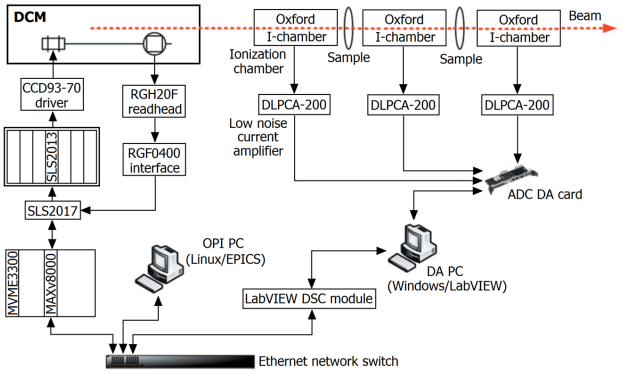

Fig. 4. Schematics of the QXAFS system.

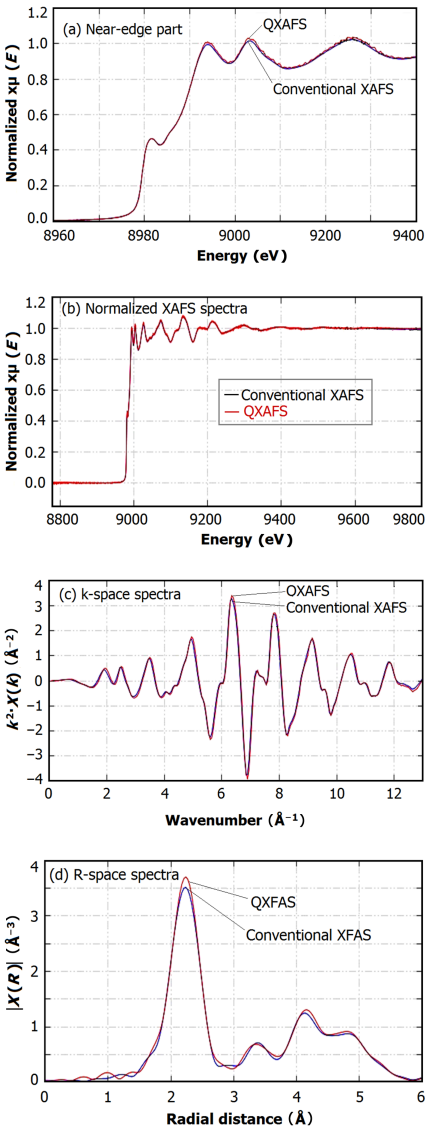

Fig. 5. (Color online) Conventional Cu K-edge XAFS spectra and the QXAFS spectra measured in 2 s with the energy range of 1.2 keV.

B. Grazing incidence XAFS

Grazing incidence X-ray absorption spectroscopy (GI-XAFS) is a powerful tool for studying surface and interface phenomena, such as adsorption, thin film growth, etc. The surface sensitivity is closely related to the penetration depth of X-rays, which amounts to a few nanometers for grazing angles below the critical angle of total reflection.

The GI-XAFS setup of BL14W1 beamline uses two slits to limit the beam size to 10–20 μm. The samples are mounted on a high-precision five-dimension sample stage, i.e. vertical and horizontal translations in micrometer precision, a goniometer to tilt the sample ($\pm 3°$) along the X-ray beam, and another goniometer to rotate ($180°$) the sample in the beam. XAFS spectra are collected in the fluorescence mode with the Si(111) DCM. It can collect data with the polarization vector parallel or perpendicular to the sample surface. The incident-beam intensity is monitored using the first gas ion chamber, while reflected beam is monitored using the second gas ion chamber for adjust the zero angle. The fluorescence emission is collected by a 4-element silicon drift detector (Fig. 6). The GI-XAFS measurements are usually dedicated for studying surface and interface structures of thin films [13–16].

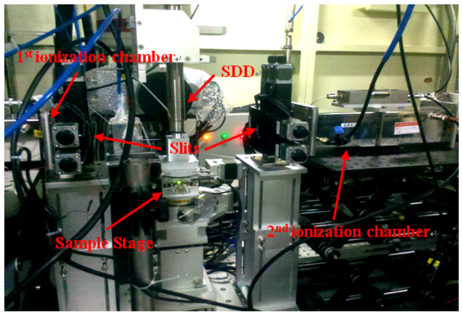

Fig. 6. (Color online) The grazing-incident XAFS setup of BL14W1.

C. X-ray emission spectroscopy

A solid state detector (SSD) or silicon drift detector (SDD) has an energy resolution of no better than 120 eV. Such an energy resolution under the fluorescence mode cannot clearly distinguish the signals within similar energy range, such as $K_{\beta_{1,3}}$, $K_{\beta'}$, $K_{\beta_{2,5}}$ and $K_{\beta''}$ of the K_β line series of 3d transition metals, but they represent different electronic structures that are sensitive to the spin, oxidation state, ligand identity, hybridization, etc.

X-ray emission spectroscopy (XES) utilizes high-index surface of crystals to achieve high energy resolution. In the experimental setup, the sample, the spherically curved crystal analyzer and the detector are arranged in the Rowland geometry to select fluorescence photons with the specific energy according to Bragg's law. Thus, XES is a powerful tool to study the electronic structure and ligand environments for 3d transition metals.

BL14W1 beamline is equipped with the XES instrument (Fig. 7(a)) based on horizontal Rowland geometry [17, 18]. For manganese compounds, high quality high resolution spectra were achieved (Fig. 7(b)).The diameter of Rowland cycle can be adjusted between 1 m and 182 mm for either high resolution or high counts. The full width at half maximum of the K_β main lines of $MnSO_4$ is about 2.5 eV and 0.5 eV with the 182 mm and 1000 mm crystal, respectively. The 1000 mm crystal resolution is of the same level of similar equipment in other beamlines (Super-XAS at PSI, FAME at ESRF).

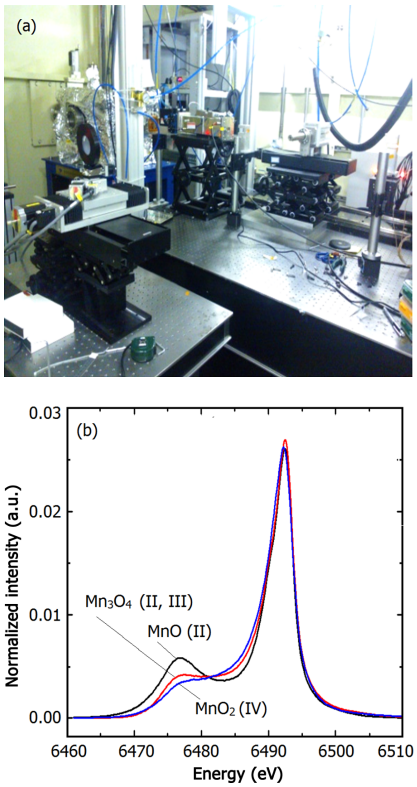

Fig. 7. (Color online) The XES set-up of BL14W1(a) and K_β line series spectra (b) of MnO, Mn_3O_4 and MnO_2 with 1000 mm crystal.

D. Focusing technique for high-pressure experiment

High-pressure is an important research field with synchrotron radiation. When SSRF began its construction, there was no effective EXAFS technique for investigation of local structures at high pressure. The typical beam spot size of 300 μm × 300 μm limits further increase of pressure. Recently, we used the Kirkpatrick-Baez optics-based focusing technique to reduce the spot size to < 50 μm × 50 μm at the sample. In this way, high pressure of ≥ 30 GPa can be obtained by diamond anvil cell for the related EXAFS study. Several groups have already carried out their high-pressure experiments at BL14W1 with fairly good results (Fig. 8).

We are also developing a polycapillary lens-based focusing technique at BL14W1. The polycapillary lens takes the advantage of large divergence of focused X-ray beam on the

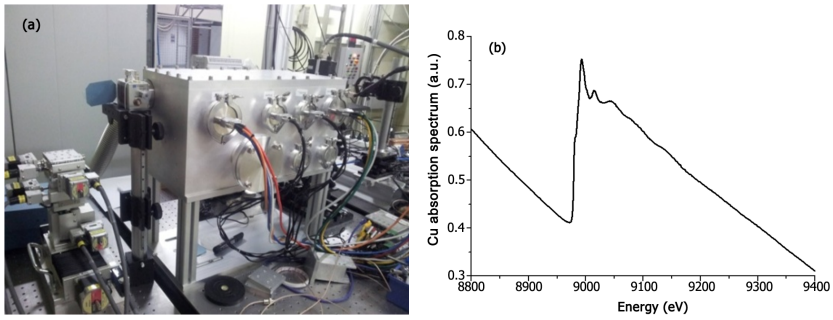

Fig. 8. (Color online) K-B focusing system (a) and the EXAFS data at 30 GPa (b).

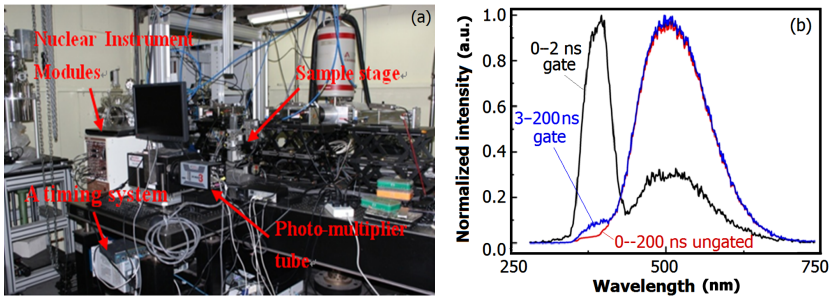

Fig. 9. (Color online) The time-resolved XEOL setup (a) and TRXEOL spectra (b) of ZnO nanowire at 0–2 and 3–200 ns gates, and 0–200 ns ungated.

sample, hence the effective suppression of diffraction peaks induced by the diamond mold. This is very useful for analyzing high-pressure XAFS data.

E. Time-resolved X-ray excited optical luminescence (TR-XEOL)

XEOL studies optical emission from a material excited through X-ray absorption. The optical emission spectrum contains information regarding the decay process of a material. At the BL14W1 of SSRF, the TR-XEOL method has be used, and implemented to measure the structure of the storage ring as a function of time (Fig. 9(a)) [19, 20].

The TR-XEOL method is based on the principle of time-correlated single photon counting techniques (TCSPC). The XEOL system consists of a spectrometer with a detector and photomultiplier tube (PMT), a timing system and a set of Nuclear Instrument Modules (NIM). The optical spectrometer is an energy dispersive instrument, allowing for faster collection of XEOL spectra. A zinc oxide (ZnO) nanowire, which has a fast optical luminescent process at the wavelength of 390 nm, converts the X-ray pulses into optical luminescent pulses. Time structure of the storage ring was indirectly measured by detecting and recording time stamps of the luminescent pulses according to the TCSPC principle. Figure 9(b) shows the TR-XEOL spectrum of the ZnO nanowire at time gates of 0–2, 3–200 and 0–200 ns. The results demonstrate that the time resolution of the TR-XEOL system is less than 1 ns.

F. Sample Environments

In-situ XAFS can probe structure of a material under its working condition. As the number of XAFS users in SSRF increases, traditional static XAFS characterization is unable to meet the heavy user demands. Some *in-situ* high and low temperature cells have been developed to facilitate the users at BL14W1 (Table 2). Figure 10 shows composition of the *in-situ* cells of high-low temperature and pressure. The users can use them in cooperation with the beamline scientists.

TABLE 2. Parameters of *in-situ* cells

Temperature	Pressure (Pa)	Reaction gas	Mode[a]
300–700 K	0.1–1 M	√	T, F
77–400 K		√	T
77–800 K	$8 \times 10^{-3} - 0.2$ M	√	T, F
4–300 K	—	—	T

[a] T, transmission; F, fluorescence

IV. EXPERIMENTAL RESULTS OF BL14W1 STATION

To illustrate performance of the XAFS station, XAFS measurement in transmission mode was made on a standard copper foil. Data for Figs. 11–13 was analyzed and plotted using the Athena software (Bruce Ravel & Matt Newville, 2008). Copper is suitable for characterizing standard XAFS experiments. Figure 11 shows the Cu EXAFS data and Fig. 12

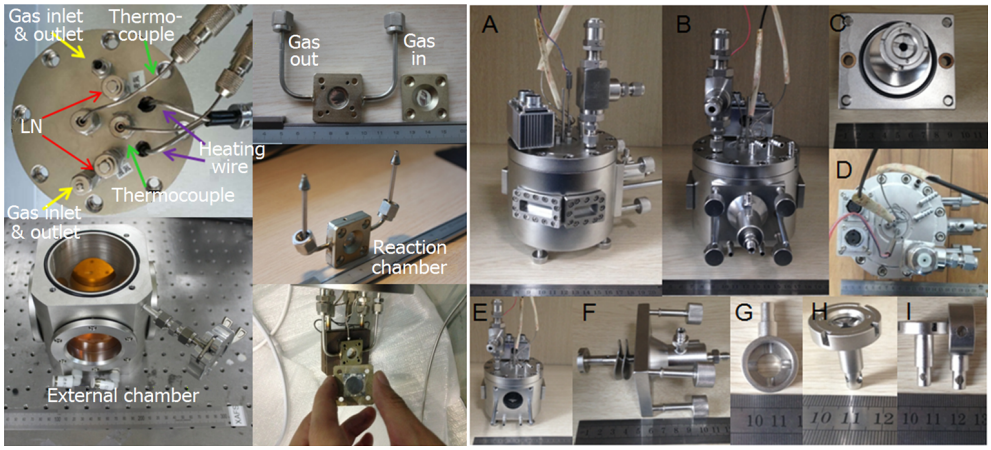

Fig. 10. (Color online) *In-situ* cell of high-low temperature and pressure.

shows the Cu EXAFS data with the k^3-weighted in k space. From the Cu XANES spectrum, the distinctly resolved pre-edge feature in the Cu spectrum at 8981.3 eV (Fig. 13), the energy resolution at the copper K edge is about 1.3 eV, which is sufficient for near-edge studies and comparable to other equivalent beamlines. The quality of EXAFS data can extend out to $k = 16$–17 Å^{-1}.

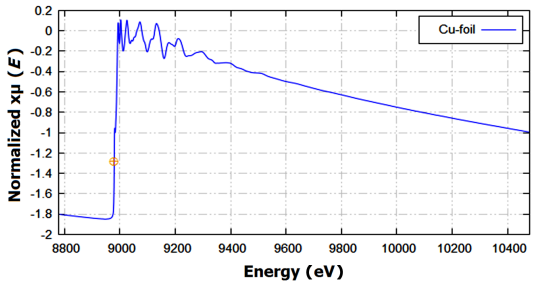

Fig. 11. (Color online) X-ray absorption spectrum of 7 μm-thick Cu reference foil (EXAFS Co.).

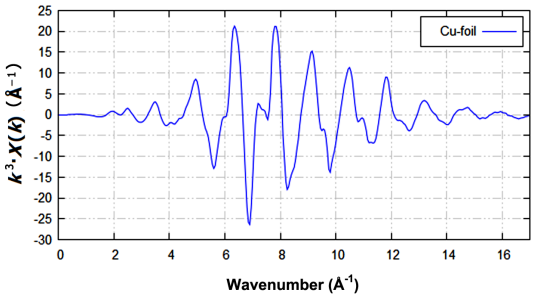

Fig. 12. (Color online) Cu foil in k space, k3-weighted.

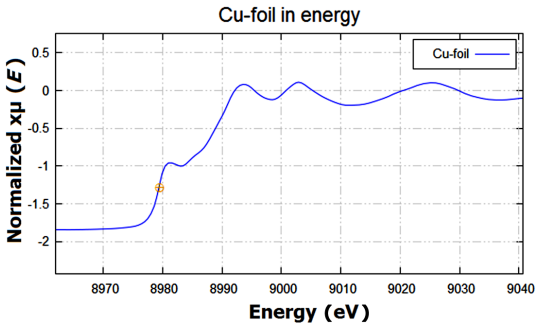

Fig. 13. (Color online) XANES spectrum of Cu K edge, the distinct resolved pre-edge feature at 8981.3 eV.

V. CONCLUSION

The XAFS beamline at SSRF is a powerful platform to investigate the local structure of materials for research in fields of physics, chemistry, materials, environmental science and so on. At present, standard XAFS data can be collected in transmission and fluorescence yield modes. In addition, quick-scanning XAFS method (QXFAS), X-ray emission spectroscopy (XES),grazing incidence XAFS (GIXAFS), high pressure XAFS and time-resolved X-ray excited optical luminescence methods will be gradually available to users in the future.

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