NEW APPARATUS, UPGRADES & METHODOLOGY

Development of quick-scanning X-ray absorption spectroscopy system with servo-motor-driven channel-cut monochromator

Time-resolved quick-scanning X-ray absorption fine structure (QXAFS) techniques are powerful tools for *in situ* investigations of the dynamics of physical/chemical reactions that occur over time scales of seconds or shorter. Many QXAFS techniques have been developed over the last two decades. Frahm *et al*. acquired extended X-ray absorption fine structure (EXAFS) spectra with a repetition rate of up to about 40 Hz using a cam-driven monochromator at the undulator beamline at DESY [1]. Uruga *et al*. measured EXAFS spectra with a temporal resolution of 50 ms using a compact Si channel-cut crystal and a quasi-monochromatic helical undulator radiation over the energy range 8 – 17 keV [2].

A dedicated beamline **BL33XU** (Toyota beamline) commenced operation in 2009. It is designed to be used to research a wide variety of new materials for sustainable vehicle technologies, such as automobile exhaust catalysts, secondary batteries, and fuel cells. In studies of such functional materials, *in situ* time-resolved measurements are essential for determining the mechanisms that give rise to their functions. To realize this goal, we designed a novel QXAFS system with a temporal resolution of 10 ms [3].

A higher photon flux is required to obtain better quality spectra that can be used for XAFS analysis with a short scanning time. We employed a tapered undulator to obtain a high photon flux and to increase the energy bandwidth of XAFS measurements by tapering the gaps in the undulator magnet array. To realize 10 ms QXAFS measurements using intense undulator radiation, we designed a QXAFS monochromator system that consists of a compact channel-cut Si crystal and a high-speed direct-drive AC servo-motor.

The light source is a tapered in-vacuum undulator, which is the first tapered undulator installed at SPring-8. Figure 1 shows the spectral fluxes of the fundamental harmonic measured on the X-ray beam axis for an average gap width of 14 mm and two different taper ratios. The measured energy widths were 600 and 1700 eV for taper ratios of 0.5 mm/4.5 m and 2.0 mm/4.5 m, which are, respectively, suitable for XANES and EXAFS measurements.

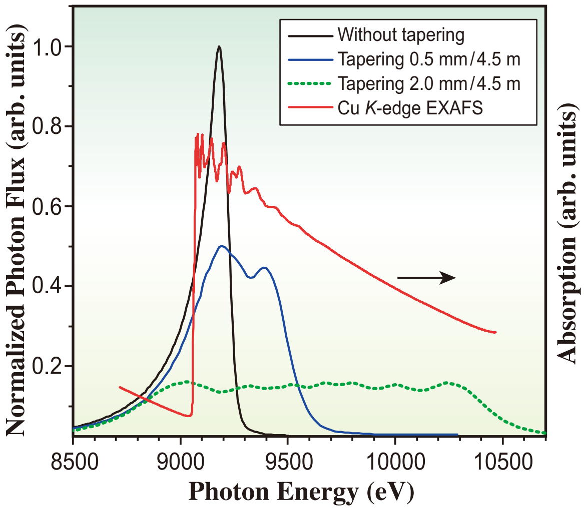

Fig. 1. Measured on-axis spectral flux of the fundamental harmonic of the tapered in-vacuum undulator (average gap width: 14 mm) and a Cu *K*-edge XAFS spectrum of a Cu foil obtained with 2.0 mm/4.5 m tapering.

The minimum temporal resolution of QXAFS is limited by the maximum oscillation frequency of the crystal, which depends on the inertia of the crystal and holders and on the torque of the servo motor. The monolithic Si channel-cut crystal was designed to reduce the rotational inertia of high-frequency mechanical oscillations. The crystal has a narrow 3-mm-wide gap between the reflecting planes, which enables the crystal to be downsized to 70×70×70 mm^3. The reflecting planes were fabricated inside the crystal by hollowing out the silicon block. The crystal is almost axially symmetric about the rotation axis of the monochromator. The first and second reflecting planes are arranged to be geometrically equivalent so that they are uniformly cooled, which reduces the throughput loss.

Figure 2 shows a diagram of the interior of the servo-motor-driven monochromator. The channel-cut crystal is clamped on both sides by liquid-nitrogen-cooled copper blocks. This arrangement enables the crystal to be tightly held by the cooled blocks to withstand high-frequency oscillations, and it reduces deformation of the reflecting plane owing to the clamping force.

The crystal holder is rotated by a high-precision, high-torque AC direct-drive servo motor (Nikki Denso, D250-100-F) installed outside the vacuum vessel. A magnetic fluid rotary feedthrough seal unit (Rigaku Mechatronics) is used to transfer the rotary motion of

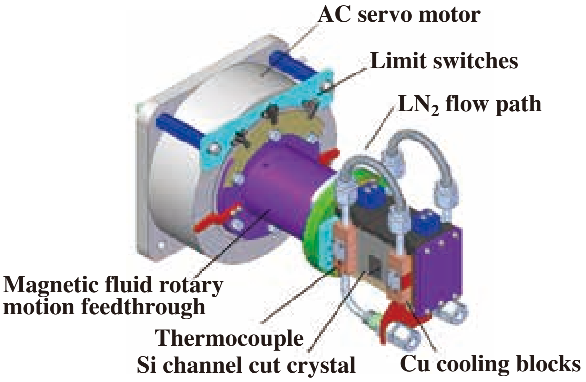

Fig. 2. Schematic of interior of the direct-drive servo-motor-driven monochromator.

the servo motor to the crystal holder inside the vacuum vessel. The angular resolution of the monochromator is 10^{-4} degrees (0.36 arcsec), which is determined by the resolution of the servo-motor internal encoder.

Two monochromators are aligned in tandem in the first experimental hutch of BL33XU. The monochromators with Si(111) or Si(220) crystals cover energy ranges of 4.0 – 28.2 keV and 6.6 – 46.0 keV, respectively. The Si(111) and Si(220) monochromators can be interchanged on the X-ray beam axis by using vertical translation stages without breaking the vacuum in the vessels.

A control system was constructed for three XAFS scanning modes with different temporal resolutions. Table 1 shows the specifications of these three scanning modes. For the continuous scanning mode, the undulator gap is tapered and the angular velocity of the servo motor has a triangular wave. However, for scanning faster than 0.5 Hz (i.e., a temporal resolution of less than 1 s), the servo motor cannot be oscillated with a triangular wave due to the inertia of the crystal and the holder; instead, it is oscillated with a sinusoidal wave (termed the super quick scan mode). For XAFS scans that require long measurement times, the servo motor is rotated incrementally and the undulator gap is not tapered; rather, it is tuned to maximize the photon flux at each measurement point (step scan mode). These three scan modes can be switched in a very short time and the energy ranges of scans, the starting angles of oscillations, and the frequencies can be adjusted instantly. The control and measurement system is fully operated by a PC using user-friendly application software written in LabVIEW.

Table 1. Specifications of three XAFS scanning modes available with the system.

Mode	Super quick scan	Continuous scan	Step scan
Temporal resolution	< 1 s	1 s – 1 min	> 1 min
Motion pattern	Sinusoidal wave	Triangular wave	Incremental
Undulator gap	Tapered	Tapered	Non-tapered
Data acquisition	ADC	Counter /ADC	Counter

The QXAFS system was characterized by conducting performance tests in the superquick scan mode. Figure 3 shows XANES spectra of a Cu foil measured at different scan speeds with an angular range of 0.2° using the Si(111) monochromator. The undulator gap had a taper ratio of 0.5 mm/4.5 m. The pre-edge spectrum (around 8980 eV), which represents metallic Cu, is clearly visible even in the 50 Hz oscillation spectra. The signal-to-noise ratio of the 50 Hz oscillation spectra is sufficiently high for analysis owing to the high incident X-ray flux from the tapered undulator and to the low-noise data acquisition system. These results indicate that our QXAFS system (including the light source, beamline optics, and measurement system) operates effectively with a temporal resolution of up to 10 ms.

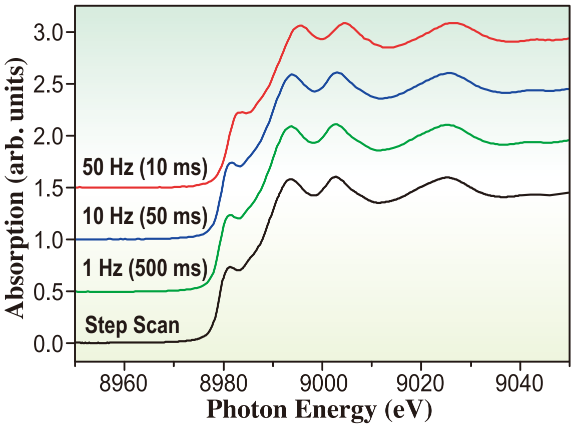

Fig. 3. Cu *K*-edge XANES spectra of 6-μm-thick Cu foil measured in superquick scan mode using the Si(111) channel-cut crystal (undulator gap taper: 0.5 mm/4.5 m). A step scan spectrum is also shown for comparison.

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References

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[3] *T. Nonaka, K. Dohmae, T. Araki, Y, Hayashi, Y. Hirose, T. Uruga, H. Yamazaki, T. Mochizuki, H. Tanida and S. Goto: Rev. Sci. Instrum.* ***83*** *(2012) 083112.*