Quick-scanning x-ray absorption spectroscopy system with a servo-motor-driven channel-cut monochromator with a temporal resolution of 10 ms

T. Nonaka,[1,a)] K. Dohmae,[1] T. Araki,[1] Y. Hayashi,[1] Y. Hirose,[1]
T. Uruga,[2] H. Yamazaki,[2] T. Mochizuki,[2,3] H. Tanida,[2] and S. Goto[2]
[1]*Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan*
[2]*JASRI/Spring-8, 1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan*
[3]*Toyama Corp., Zama, Kanagawa 228-0003, Japan*

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We have developed a quick-scanning x-ray absorption fine structure (QXAFS) system and installed it at the recently constructed synchrotron radiation beamline BL33XU at the SPring-8. Rapid acquisition of high-quality QXAFS data was realized by combining a servo-motor-driven Si channel-cut monochromator with a tapered undulator. Two tandemly aligned monochromators with channel-cut Si(111) and Si(220) crystals covered energy ranges of 4.0–28.2 keV and 6.6–46.0 keV, respectively. The system allows the users to adjust instantly the energy ranges of scans, the starting angles of oscillations, and the frequencies. The channel-cut crystals are cooled with liquid nitrogen to enable them to withstand the high heat load from the undulator radiation. Deformation of the reflecting planes is reduced by clamping each crystal with two cooling blocks. Performance tests at the Cu K-edge demonstrated sufficiently high data quality for x-ray absorption near-edge structure and extended x-ray absorption fine-structure analyses with temporal resolutions of up to 10 and 25 ms, respectively. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4746770]

I. INTRODUCTION

X-ray absorption spectroscopy is an important technique for investigating the chemical states and local environments of atoms in materials. 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.[1–10] 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.[5] Uruga *et al.* measured EXAFS spectra with a temporal resolution of 50 ms using a compact Si channel-cut crystal and a quasi-monochromatic (bandwidth: 1.5%–2.5%) helical undulator radiation over the energy range 8–17 keV.[7]

We have constructed a dedicated beamline BL33XU (Toyota beamline) at the SPring-8; this 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 auto 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.[11–13] To realize this goal, we designed a novel QXAFS system that has a temporal resolution of 10 ms and installed it at BL33XU.

A higher photon flux is required to obtain better quality spectra that can be used for x-ray absorption fine structure (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. To manage the high heat load from the undulator radiation, the Si crystal and its holder can be cooled by liquid nitrogen. To conduct XAFS measurements for various elements in the materials, we installed two monochromators to cover a wide energy range from 4.0 to 46.0 keV. This paper describes the design of the QXAFS system and presents some results of performance tests conducted at BL33XU.

II. INSTRUMENTATION

A. Light source and optics

The light source installed at BL33XU is a tapered in-vacuum undulator, which is the first tapered undulator installed at the SPring-8. The energy width of the harmonics can be increased by varying the taper ratio of the tapered undulator gap. In the undulator at BL33XU, the gaps on the exit side are wider than those on the entrance side. 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 for 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 x-ray absorption near-edge structure (XANES) and EXAFS measurements.

During XAFS measurements, higher harmonics are rejected using 1000-mm-long double upstream mirrors and 700-mm-long double downstream mirrors. All the mirrors are

a)Electronic mail: nonaka@mosk.tytlabs.co.jp.

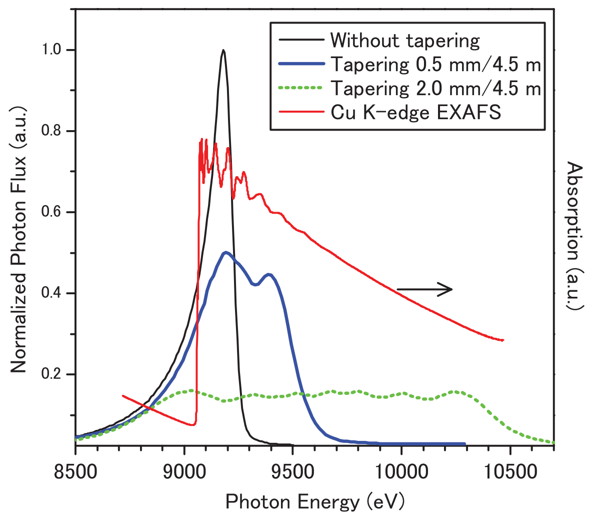

FIG. 1. Measured on-axis spectral flux of the fundamental harmonic of the tapered in-vacuum undulator (average gap width: 14 mm) and a Cu K-edge XAFS spectrum of a Cu foil obtained with 2.0 mm/4.5 m tapering.

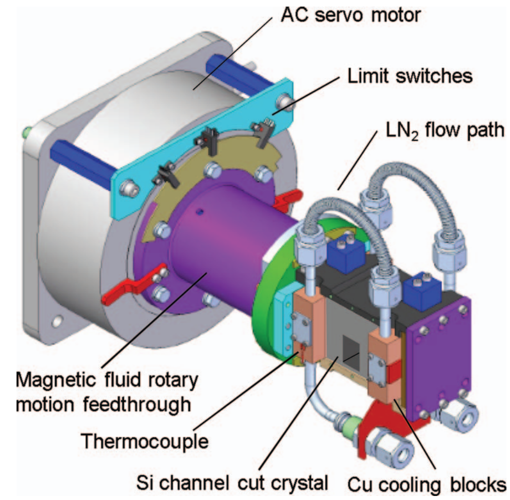

FIG. 3. Schematic of interior of the direct-drive servo-motor driven monochromator.

coated with the stripes of Pt and Rh and can be bent to focus the x-ray beam on the sample in the horizontal and vertical directions. The focused beam size was measured to be about 200 (H) $\times$ 900 (W) μm (full width at half maximum), and the total photon flux was estimated to be about 10^{13} photons/s at 12 keV.

B. QXAFS monochromator

The key components of our QXAFS system are the direct-drive servo motor and the compact channel-cut crystal, which determine the fundamental performances of the QXAFS system. 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 the 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. Figure 2 shows a schematic of the crystal. There is a 3-mm-wide gap between the reflecting planes; this gap offsets the beam height by about 6 mm, which enables the crystal to be downsized to 70 $\times$ 70 $\times$ 70 mm^3. The crystal shape was designed to allow double-bounce Bragg reflection over an angular range of

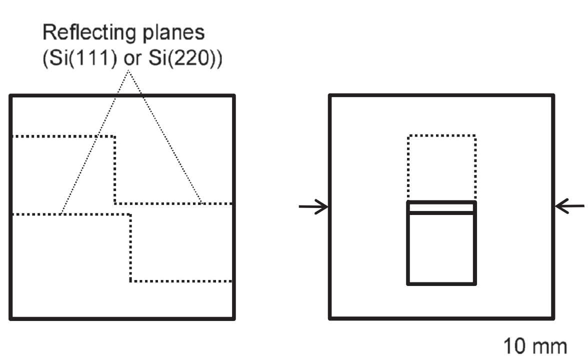

FIG. 2. Schematic of Si channel-cut crystal (side view (left) ; view from downstream (right)). Arrows indicate the surfaces that contact with the liquid-nitrogen-cooled Cu blocks.

4°–30°. 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 3 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 and the temperature is monitored by thermocouples. 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 due to the clamping force. To realize good thermal contact, 0.5-mm-thick indium sheets are inserted at the interface between the crystal and the copper blocks.

The heat load on the first reflecting plane of the crystal was estimated using the synchrotron radiation calculation code SPECTRA (Ref. 14) to be about 60 W. Finite element simulations using a commercial software ANSYS (ANSYS Inc.) predict that the slope error of the reflecting plane due to thermal deformation will be less than 5 μrad, which is sufficiently small to maintain double-bounce Bragg's conditions.

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 the servo motor to the crystal holder inside the vacuum vessel. The servo motor model was selected to maximize the oscillation frequency of the compact channel-cut crystal. The motor has a maximum torque of 186 Nm, a rated torque of 62 Nm, and a rated power of 1200 W. 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 (Fig. 4). 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

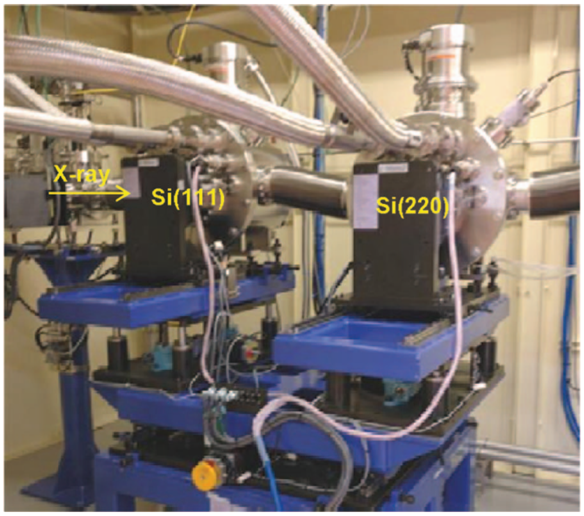

FIG. 4. Layout of Si(111) and Si(220) monochromators mounted on positioning stages.

Si(220) monochromators can be interchanged on the x-ray beam axis by using vertical translation stages without breaking the vacuum in the vessels. The vertical position of the monochromator is adjusted so that x-rays reflected from the first reflecting plane pass through the center of the channel-cut crystal at the mean energy of the QXAFS scan. The height of the x-ray beam that exits from the monochromator varies during QXAFS scans (up to 220 μm during a scan from 4.0 to 5.5 keV). However, the downstream vertical focusing mirrors are used to maintain the beam height at the focal point (i.e., the sample position).

C. Control and measurement system

A control system was constructed for three XAFS scanning modes with different temporal resolutions. Table I lists 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 between a very short time and the energy ranges of scans, the starting angles of oscillations, and the frequencies can be adjusted instantly.

TABLE I. 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

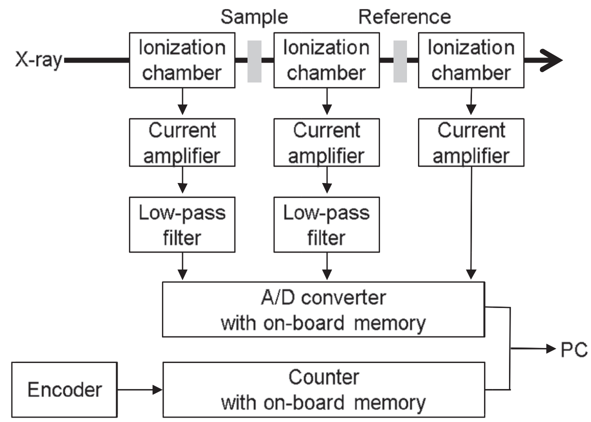

FIG. 5. Block diagram of data acquisition system for XAFS measurements in continuous and super quick scan modes.

Figure 5 shows a schematic block diagram of the data acquisition system for transmission XAFS measurements in continuous and super quick scan mode. The current signals of the ionization chambers (OKEN, S-1196A1) are amplified and converted into voltages by current amplifiers (Keithley, 428) and high-frequency electrical noise is reduced by low-pass filters (NF Corp., 3625). The processed signal of the ionization chamber is digitized and stored by a 16-bit analog-to-digital converter (ADC) board (Yokogawa, WE7272) with a maximum sampling rate of 100 kHz. The angular position of the monochromator is monitored in real time by the servo-motor internal encoder and the angular data are sampled and stored synchronously with the signals of the ionization chambers by a counter board (Yokogawa, WE7521). The data stored in the memory of the modules are transferred to a personal computer after a series of measurements. For the step scan mode or relatively slow continuous scan mode, the voltage signals of the current amplifiers are converted into frequency by voltage-to-frequency converters (Tsuji Electronics, N2VF-01) and digitized by a counter board (Arkus, Ax-cpci3901). The control and measurement system is fully operated by a PC using user-friendly application software written in LabVIEW.

III. PERFORMANCE OF THE QXAFS SYSTEM

The QXAFS system was characterized by conducting performance tests in the super quick scan mode at BL33XU. Figure 6 shows the monochromator angles measured using the servo-motor encoder for the oscillation frequencies of 50, 10, and 1 Hz with an angular range of 0.2°. The results demonstrate that the monochromator can mechanically oscillate up to a frequency of 50 Hz without generating irregular vibrations or distorting the sinusoidal waveform. The oscillations frequencies of 10 and 1 Hz comply with the control value of 0.2°, whereas the 50 Hz data deviate slightly from the control value due to a characteristic feature of the servo motor. However, this deviation is not significant for QXAFS measurements because the encoder data can be collected even for oscillation at 50 Hz.

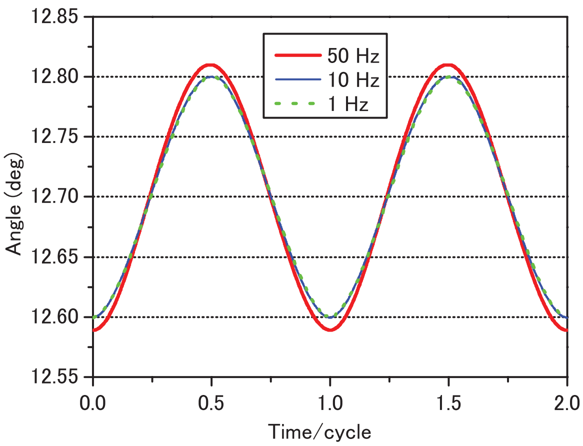

FIG. 6. Angle of monochromator measured by servo-motor encoder for the oscillation frequencies of 50, 10, and 1 Hz with an angular range of 0.2°.

Figure 7 shows XANES spectra of a Cu foil measured at different scan speeds with an angular range of 0.2° using the Si(111) monochromator. Each scan was performed from the lowest to the highest energy. The spectra are extracted from the entire cyclic-scan data and plotted. The undulator gap had a taper ratio of 0.5 mm/4.5 m. The pre-edge spectrum around 8980 eV, which is a representative of 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 due 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. However, compared to the step scan spectra, slight spectral distortions and shifts to higher energies are observed, particularly in the faster scan spectrum. These deviations may originate from the response delay of the ionization chambers, which was estimated to be several tens of microseconds. It should be possible to overcome this problem by using detectors with faster responses.

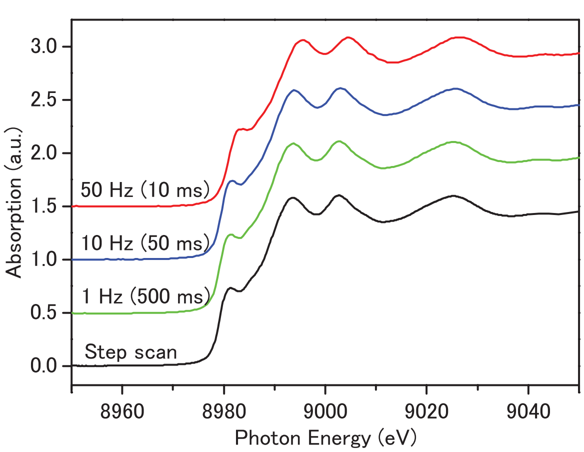

FIG. 7. Cu K-edge XANES spectra of 6-μm-thick Cu foil measured in super quick scan mode using the Si(111) channel-cut crystal (undulator gap taper: 0.5 mm/4.5 m). A step scan spectrum is also shown for comparison.

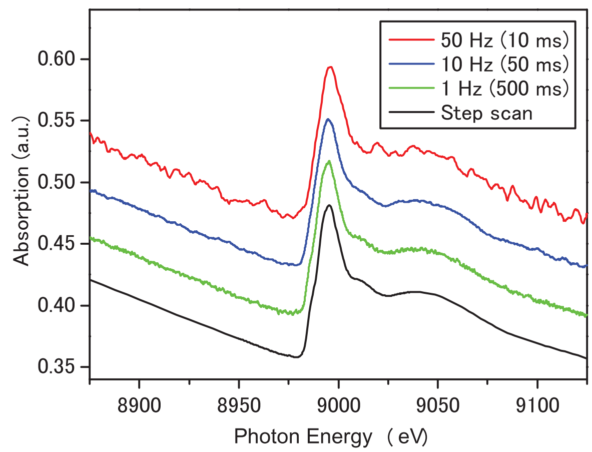

FIG. 8. Cu K-edge XANES spectra of 2.0 wt. % CuO/Al_2O_3 measured in super quick scan mode with an angular range of 0.4°.

As an example of spectra of a low-concentration sample, Fig. 8 shows XANES spectra of a 2.0 wt. % CuO/Al_2O_3 measured with an angular range of 0.4°. While the signal-to-noise ratio deteriorates with increasing scan speed, the main features of the edge structure are retained for oscillations with frequencies up to 50 Hz.

Figure 9 shows $\mu(E)$- and k^3-weighted $\chi(k)$-EXAFS spectra of a Cu foil measured with an angular range of 2.0°. The taper ratio of the undulator gap was 2.0 mm/4.5 m.

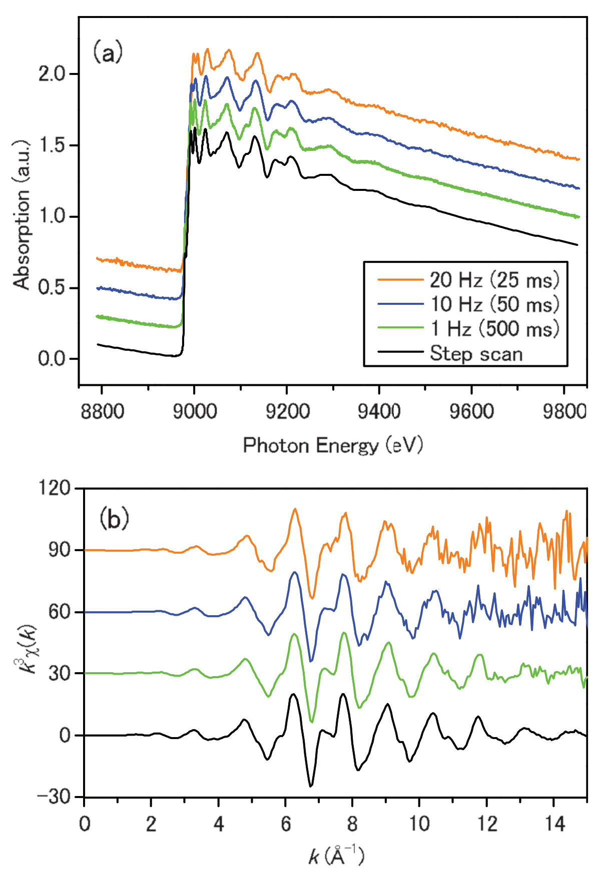

FIG. 9. (a) Cu K-edge $\mu(E)$- and (b) k^3-weighted $\chi(k)$-EXAFS spectra of Cu foil measured in super quick scan mode (undulator gap taper: 2.0 mm/4.5 m).

Background subtraction and normalization of the EXAFS spectra were performed using the software Athena.[15] The data quality of the super quick scan spectra is slightly worse than that of the step scan spectrum measured over about 20 min; this is due to the difference in their measurement times. However, meaningful EXAFS spectra can be obtained for $k < 12$ Å^{-1}, even from 20 Hz oscillation spectra. This demonstrates that the super quick scan mode of our QXAFS system is also effective for EXAFS measurements.

IV. CONCLUSION

A novel QXAFS system using a servo-motor-driven compact crystal monochromator was developed and installed in a tapered undulator beamline. The system can obtain XAFS spectra in tens of milliseconds over a wide energy range of 4.0–46.0 keV using tandemly arranged Si(111) and Si(220) monochromators. Performance tests demonstrated that the QXAFS system has a satisfactory temporal resolution, energy range, data quality, and flexibility of control system. This system has the potential to investigate the dynamics of chemical reactions of functional materials by time-resolved *in situ* QXAFS measurements.

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