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Newly Developed Experimental Facilities

1-1 Overview

Since the first beam in March 1982, we have continually constructed many beamlines and experimental stations to meet the users' requirements in the wide scientific fields, as the PF was the unique SR facility which could supply hard X-ray in Japan. In 1995, the number of the experimental stations attained to approximately 70, which much greater than the number of the scientific staff. With the limited amount of budget, there has already been difficulty in keeping the user support at a reasonable level.

Meanwhile, the SPring-8 started the operation in 1997 and it was almost sure that the PF beamline strategy should be changed, since the PF was not anymore the unique X-ray facility in Japan. Furthermore, the argument to change the beamline strategy has been accelerated with the two events; 1) the PF-AR became a dedicated machine for SR usage and the experimental possibility was expanded with a certain amount of budget to construct N and NW experimental halls in 2001, and 2) the reinforcement of the straight sections at the PF ring was accomplished with the lattice renewal in 2005. With the 2nd event, the two long and five middle straight sections were elongated to 9 m and ~5 m, respectively, and 4 short straight sections were newly produced for installation of short period and small gap undulators to supply hard X-ray photons.

Photon Factory started beamline refurbishment program in 2005, based on a new beamline strategy, attained after a severe discussion including PF user community, as follows; 1) budget and manpower are to be concentrated mainly in insertion device beamlines, 2) competent and high-demand bending magnet beamlines are supported, and less active ones are decommissioned, 3) five long and medium straight sections of the PF ring are dedicated to VUV-SX activities, other two and four short straight sections to hard X-ray research, and 4) high energy and time-resolved hard X-ray experiments are moved to PF-AR.

Among five long and medium straight sections, BL-28, BL-16 and BL-13 were constructed for hybrid usage between soft and hard X-ray regions, in 1990s. These three beamlines have been completely renewed for predominant usage in soft X-ray region. BL-28 has been renewed as a soft X-ray beamline equipped with a high resolution angle resolved photoelectron spectrometer in 2004. A fast polarization switching spectroscopic VSX beamline was constructed with two APPLE-II undulators at BL-16. Reconstruction of BL-13 was carried out to promote the study of functional organic materials by photoelectron spectroscopy. The present status of the last two beamlines is described below.

Short period and small gap undulators have been installed at three short straight sections, BL-3 for materials science, and BL-1 and 17 for macromolecular crystallography. Among three BLs, BL-1 was constructed with funding by the Target Protein national project, where they can analyze small crystal samples less than 10 μm with single anomalous dispersion technique for sulfur atoms or light atoms by means of 4-keV soft X-rays. In the last short straight section, we are planning to construct a complex analysis beamline using small angle X-ray scattering and EXAFS at BL-15. For this program, we started to transfer the existing three X-ray experimental stations.

In PF-AR, the opportunity for SR usage was increased with new equipment in N and NW experimental hall in the early 2000s. Furthermore, NE experimental hall, the oldest one at PF-AR, has been completely renewed in 2008. Hybrid usage of AR-NE1 was dissolved, and a new pharmaceutical beamline was constructed at NE3.

The number of experimental stations was 67 in 2005, when the beamline refurbishment program was started. The beamline refurbishment program including the above-mentioned manipulation results in 52 experimental stations after 13 newly constructed and relocated experimental stations and 28 decommissioned ones. This number 52 is even far from the index, 30-40, which was suggested by the Photon Factory Review Committee held in March 2006, and PF will make a further effort to promote the beamline refurbishment program to approach to the index. So far we have been concentrated on the insertion device beamlines, we call it the first phase of the PF beamline refurbishment program, and we will initiate the second phase program where we will pay attention also on the bending beamlines; merging and decommissioning will result in the reduction of the number of experimental stations, consequently, the resource, budget and manpower, may be invested effectively on competent and high-demand beamlines. As a result of the first phase program, five undulator-based beamlines are now used solely for the VSX region, however, some of the insertion device should be renewed so that the newly constructed beamline can be used in their full performance.

1-2 BL-1A: A Long-Wavelength Macromolecular Crystallography Beamline

Recent developments in single anomalous dispersion (SAD) phasing techniques are helping to solve macromolecular crystal structures using light atoms

such as sulfur or phosphorus. Longer wavelength beams ranging from 1.7 Å to Cr K-edge (~2.3 Å) have been used mainly for data collection to enhance the weak anomalous signals [1]. The method is attractive for de novo structure solutions without any derivatives, including membrane proteins and macromolecular complexes, for which heavy atom or selenomethionine derivative crystals are difficult to prepare.

We have developed the BL-1A synchrotron beamline specifically for long-wavelength SAD experiments. The beamline is designed to take full advantage of long-wavelength X-ray beams of around 3 Å to enhance anomalous signals. The design and optics of the beamline were described in the previous report [2]. In this fiscal year we built a 'control cabin' adjacent to the experimental hutch for users to prepare samples, control diffraction experiments and process the data (Fig. 1). Beam position monitors were installed to record the intensity and position of the beam online, which will be used as a part of the beam position feedback system in future. A booth surrounding the diffractometer equipped with a temperature controller was introduced in the ex-

perimental hutch to precisely maintain the temperature of the diffractometer, thus helping to stabilize the beam (Fig. 2).

Diffraction experiments using the wavelength of 2.7 Å were performed against various protein or nucleic acid crystals. Some of the crystals were mounted in the 'mother-liquor free' condition following the method developed by Hokkaido University [3,4] to decrease the background noise and anisotropic absorptions. Structural solutions by the sulfur-SAD method were obtained for some protein crystals. As a preliminary result, Dr. Zhi-Jie Liu of the Chinese Academy of Sciences solved a protein of 40 kDa with 14 sulfurs (4 Met and 10 Cys) using the 3 Å resolution data.

REFERENCES

- [1] K. Djinovic Carugo, J. R. Helliwell, H. Stuhrmann and M. S. Weiss, *J. Synchr. Rad.*, **12** (2005) 410.
- [2] *Photon Factory Activity Report* **27** (2009) 78
- [3] Y. Kitago, N. Watanabe and I. Tanaka, *Acta Cryst. D*, **61** (2005) 1013.
- [4] Y. Kitago, N. Watanabe and I. Tanaka, *J. Appl. Cryst.*, **43** (2010) 341.



Figure 1
Overview (left) and inside (right) of the 'control cabin'

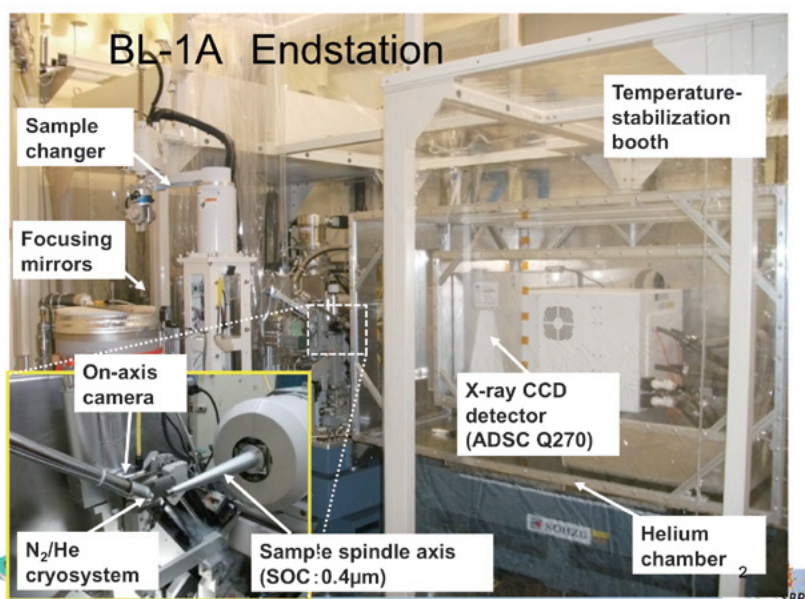


Figure 2
Inside the experimental hutch of the BL-1A. The diffractometer is surrounded by the temperature stabilization booth.

1-3 BL-6A: Reconstruction for Small Angle X-Ray Scattering Beamline

BL-6A, which is dedicated for small angle X-ray scattering (SAXS) experiments and to which the activities carried out at BL-15A were moved, is under reconstruction. BL-15 is the last site for the X-ray short-gap undulator at the PF-ring and we have started discussions on renewing BL-15 as a high-brilliance beamline.

BL-15A was built about 30 years ago for time-resolved studies of small-angle diffraction from contracting muscles. The optics consist of a bent flat mirror and a triangle bent asymmetric-cut monochromator for vertical and horizontal focusing, respectively. It can produce a point focus spot with a high spatial resolution and the intensity necessary for 2D-SAXS-WAXS experiments. Thanks to its good point focus, the beamline is still widely used for 2D-SAXS and 2D-WAXS. To keep and facilitate such high 2D-SAXS-WAXS activities, we decided to relocate BL-15A to BL-6A where the current BL-15A settings can be transferred.

Figure 3 shows the schematic layout of BL-6A. The front-end is partly renewed. A new water-cooled mask for splitting into BL-6A and 6C at 3.925 m from the source point provides a 2.04-mrad white beam. A focusing mirror is installed at 10 m in order to obtain a high-brilliance beam while eliminating higher energy X-rays in the beam. The ULE plane mirror has a 1.1-m-long reflecting surface. A synchrotron radiation beam is focused by the mirror at a glancing angle of 3.0 mrad (a critical wavelength of 1.21 Å). A single bounce monochromator is located at 12.2 m. An optical bench equipped with a cylindrically curved monochromator for horizontal focusing is installed inside the monochromator chamber. A triangular Ge(111) crystal with an asym-

metric angle of 8.0 degrees is used as a monochromator crystal for optimum focusing of the beam at 1.5 Å. The optical bench is provided with a slit system and a horizontal 2θ table is used for mounting the SAXS camera stage. The focal point is 14.8 m at the surface of the detectors which are set on the newly designed detector stage. In comparison, the optics of the existing BL-15A are mirror at 13 m, monochromator at 17.5 m and focal point at 22.1 m. Thus, even though it is shorter, the BL-6A design is almost the same as the existing BL-15A.

The reconstruction of BL-6A began in FY2009. BL-6A had been dedicated for structural biology for many years, but it was shut down in March 2010 and the hutch and beamline component were scrapped immediately. The experimental hutch, deck, electrical power supply and other facility work were completed in FY 2010 (Fig. 4). The mirror bender, branch beam shutter (BBS) and some beamline components will be installed before the summer shutdown of 2011. During the shutdown, BL-15A will be closed and the other components



Figure 4
BL-6A experimental hutch at the end of FY2010.

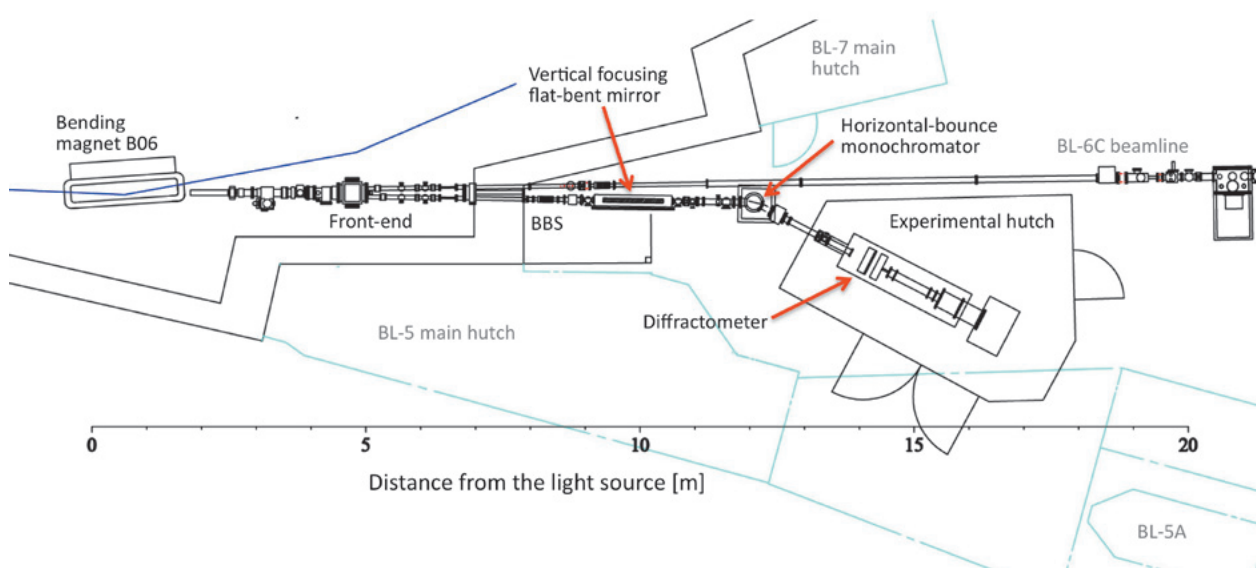


Figure 3
Schematic layout of the BL-6A.

and experimental apparatus of BL-15A will be moved to BL-6A. After short commissioning at the beginning of 2011 autumn operation, BL-6A will be opened to mainly BL-15A users.

1-4 BL-13A: A New VUV-SX Undulator Beamline for the Study of Organic Thin Films Adsorbed on Surfaces

A new vacuum ultraviolet and soft X-ray (VUV/SX) undulator beamline (BL-13A) was opened to users on January 29, 2010. BL-13A is mainly dedicated to studies on organic thin films adsorbed on well-defined surfaces using angle-resolved photoelectron spectroscopy (ARPES), high resolution X-ray photoelectron spectroscopy (HR-XPS) and X-ray absorption spectroscopy (XAS).

Figure 5 shows typical undulator spectra measured using a silicon photodiode. On the basis of a series of undulator spectra measured for undulator gaps of 100–210 mm, the photon flux for an exit-slit width of 30 μm is estimated to be 10^{11} – 10^9 photons/s for 30–1,200 eV. Figure 6 shows the XAS of gaseous N_2 in the region of the $\text{N } 1s \rightarrow \pi^*$ excitation using the 1,000 lines mm^{-1} varied-line spherical grating (VLSG) at the exit-slit width of 30 μm . Based on the data, the photon-energy resolution ($E/\Delta E$) is estimated to be about 10,000 at $h\nu = 401$ eV. A typical spot size at the first focus with the first post-focusing mirror is estimated to be about $210 \times 40 \mu\text{m}$ (horizontal \times vertical) for an exit-slit width of 40 μm . Photon-energy drift is $\leq \pm 0.02$ eV at $h\nu = 244.39$ eV (Fig. 7). An ultrahigh vacuum chamber equipped with an electron-energy analyzer (Gamma Data / Scienta, SES 200) is used as the main end station for ARPES, HR-XPS and XAS measurements (Fig. 8).

Several experiments were carried out at BL-13A. Prof. J. Yoshinobu, Dr. S. Yoshimoto, Mr. K. Mukai (The Univ. of Tokyo) *et al.* measured high-resolution XPS

and high-resolution XAS of organic molecules adsorbed on surfaces. Dr. K. Ozawa (Tokyo Inst. of Tech.) *et al.* investigated the surface electronic structures of ZnO surfaces adsorbed with organic molecules by ARPES. Dr. T. Sakurai (Tsukuba Univ.) *et al.* studied electronic structures of the interfaces of metal and organic thin films used for organic solar cells. Dr. T. Nishi, Prof. K. Sakamoto *et al.* (Chiba Univ.) measured XPS of 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (TNAP) adsorbed on Bi(001). Prof. K. K. Okudaira *et al.* (Chiba Univ.) measured XAS of organic thin films. Prof. Y. Hasegawa (The Univ. of Tokyo), Prof. T. Eguchi (Keio Univ.), Prof. T. Okuda (Hiroshima Univ.) *et al.* started synchrotron-radiation-assisted scanning tunneling microscopy (SR-STM) experiments. Prof. H. Kondoh, Dr. M. Yoshida *et al.* (Keio Univ.) began core-hole clock spectroscopy measurements of organic molecules adsorbed on surfaces.

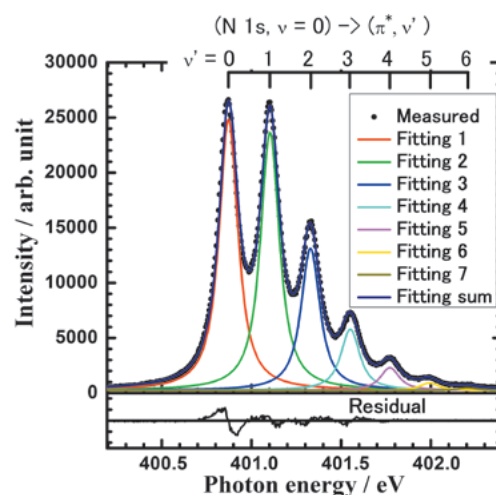


Figure 6 X-ray absorption spectrum of gaseous N_2 in the region of the $1s \rightarrow \pi^*$ excitation, using the 1,000 lines mm^{-1} VLSG for an exit-slit width of 30 μm (solid circles in the upper panel). The solid lines in the upper panel represent the fitting curves using Voigt functions. Based on the data, the photon-energy resolution ($E/\Delta E$) is estimated to be about 10,000 at $h\nu = 401$ eV [4].

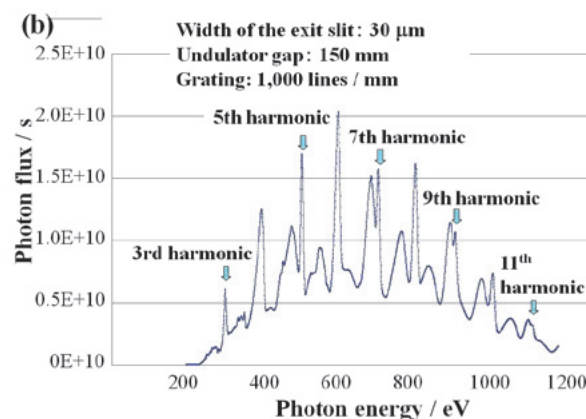
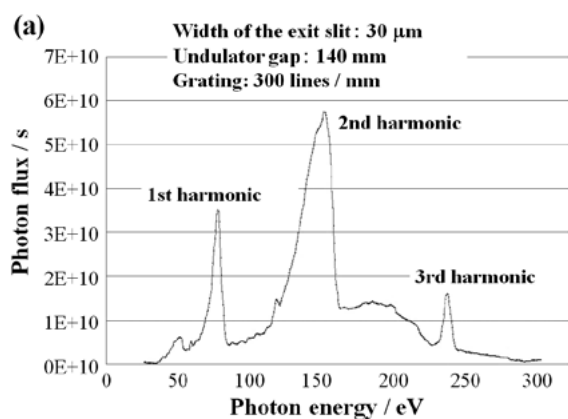


Figure 5 Typical undulator spectra measured by a silicon photodiode for (a) 300 and (b) 1,000 lines mm^{-1} VLSGs with an exit-slit width of 30 μm [4].

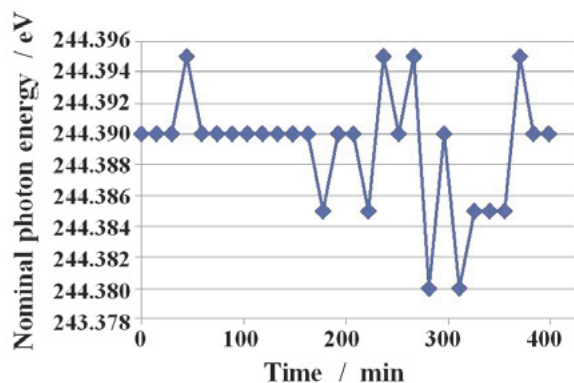


Figure 7
Photon-energy drift at the $2p_{3/2} \rightarrow 4s$ excitation of gaseous Ar using the 300 lines mm^{-1} VLSG for an exit-slit width of 30 μm [4].

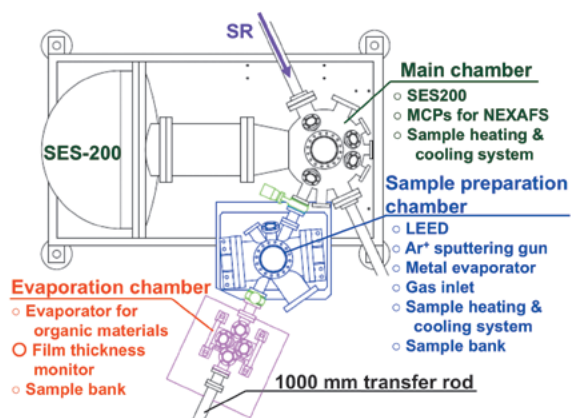


Figure 8
An ultrahigh vacuum chamber equipped with an electron-energy analyzer (Gamma Data / Scienta, SES 200) used as the main end station of BL-13A.

REFERENCE

- [4] A. Toyoshima, H. Tanaka, T. Kikuchi, K. Amemiya, and K. Mase, *J. Vac. Soc. Jpn.*, **54** (2011) 580.

1-5 BL-16A: Development of Fast Polarization Switching

A fast polarization switching technique in the soft X-ray region is being developed at BL-16A [5], with financial support from the Quantum Beam Technology Program of MEXT. Two tandem APPLE-II type undulators are set to different polarizations such as right- and left-hand circular polarizations, and polarization switching is realized by modulating the electron orbit through the undulators [6]. After installation of the second undulator in the summer of 2010, commissioning started in the autumn of 2010 (Fig. 9).

The first step in the commissioning is fine adjustment of the X-ray light paths for two undulators. A misalignment in the vertical direction would result in a difference in the X-ray energies downstream of the monochromator for the different polarizations, while that in the horizontal direction would lead to different spot positions at the sample. The electron orbit through each undulator was aligned with a few μrad precision,

by scanning an aperture upstream of the beamline and checking the intensity and energy distribution of the undulator radiation.

Then we tried to take the X-ray magnetic circular dichroism (XMCD) data from a Ni thin film by adopting the switching between the right- and left-hand circular polarizations. Variation in the X-ray intensity emitted from two undulators is shown in Fig. 10. There are two maxima in the X-ray intensity for each 100 ms, which correspond to the different polarizations from the two undulators. Moreover, the normalized sample current, I/I_0 , shows a clear change according to the change in the polarization, which directly indicates the existence of the XMCD signal. The XMCD spectrum is obtained from these data by adopting the lock-in analysis at each photon energy as given in Fig. 11.

The XMCD spectrum taken by using the polarization switching (AC mode) is compared to that taken in the conventional method (DC mode) in Fig. 11. The overall spectrum shape is almost identical for both modes, confirming the feasibility of the polarization switching technique. Moreover, the noise level in the AC mode is much smaller than 0.1%, thus enabling the detection of a tiny XMCD signal. This technique will be applied to studies on magnetic materials for spintronics devices. In addition, switching between horizontal and vertical

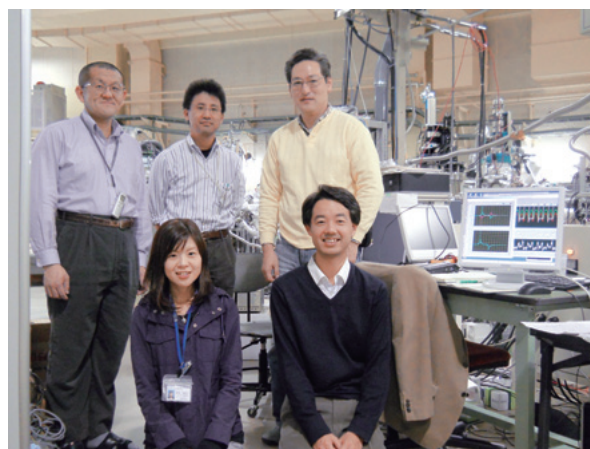


Figure 9
Commissioning of the fast polarization switching at BL-16A.

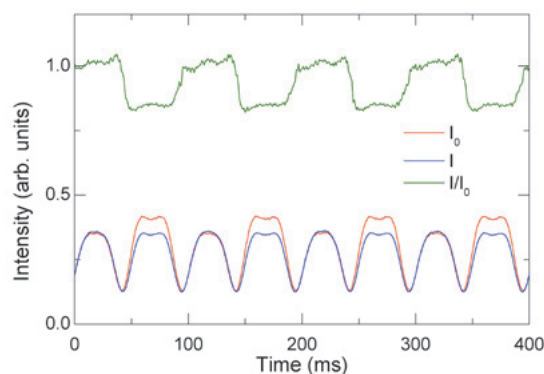


Figure 10
Variation of X-ray intensity (I_0), sample current (I), and their ratio (I/I_0) during the switching between the right- and left-hand circular polarizations at 10 Hz.

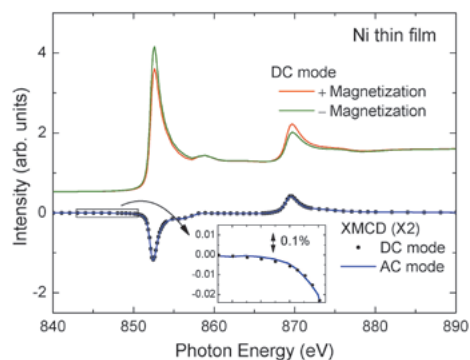


Figure 11
Ni L-edge XMCD spectra for a Ni film taken by reversing sample magnetization before each spectrum measurement with fixed X-ray polarization (DC mode) and by switching the X-ray polarization at 10 Hz with fixed magnetization (AC mode).

linear polarizations is also possible, which enables real-time observation of the structural changes of adsorbed molecules during the surface chemical reactions, by combining with a wavelength-dispersive X-ray absorption spectroscopy technique [7].

REFERENCES

- [5] K. Amemiya, A. Toyoshima, T. Kikuchi, T. Kosuge, K. Nigorikawa, R. Sumii and K. Ito, *AIP Conf. Proc.* **1234** (2010) 295.
- [6] T. Muro, T. Nakamura, T. Matsushita, H. Kimura, T. Nakatani, T. Hirono, T. Kudo, K. Kobayashi, Y. Saitoh, M. Takeuchi, T. Hara, K. Shirasawa, H. Kitamura, *J. Electron Spectrosc. Relat. Phenom.*, **144-147** (2005) 1101.
- [7] K. Amemiya, H. Kondoh, A. Nambu, M. Iwasaki, I. Nakai, T. Yokoyama and T. Ohta, *Jpn. J. Appl. Phys.* **40** (2001) L718.