

BL12XU NSRRC ID

1. Overview

BL12XU is one of the two contract beamlines between National Synchrotron Radiation Research Center (NSRRC, Taiwan) and Japan Synchrotron Radiation Research Institute (JASRI). BL12XU has an undulator source and two branches of the mainline and a sideline (see Fig. 1). The mainline has been fully operational since 2001 and used by many domestic / foreigner scientists. Inelastic X-ray Scattering (IXS) experiments were mainly performed in BL12XU and several other experiments, e.g., time-resolved high-resolution diffraction using a laser, were also carried out. The side line is dedicated to Hard X-ray Photoelectron Spectroscopy (HAXPES) and has been in operation since 2009.

2. Mainline

2-1 Instrumentation

We made several developments of instrumentation, such as high resolution IXS optics and 20 keV IXS spectrometer. Also, we have installed a high-pressure, high temperature furnace for IXS studies on supercritical fluid. The following is a short description of the high-resolution optics.

- **5 × 32-ch strip Si detector for high-resolution NIXS:** We developed a 32 channel strip Si detector last years, so that a 25 meV resolution was achieved along with single spherical crystal analyzer. Now we attempt to make the detector compatible with multi analyzer system to enhance the count rate. The new stripe detector has 5 wafers positioning in a ‘fan’ shape, detecting the reflections from 5 analyzers. We tested the detector and confirmed the outputs. More critical tests will be performed using a high-resolution monochromator. This project is conducted with K.-L. Yu and D.-H. Lee.

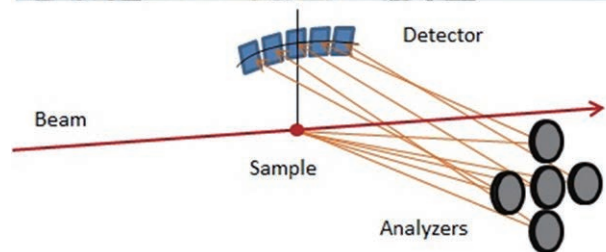
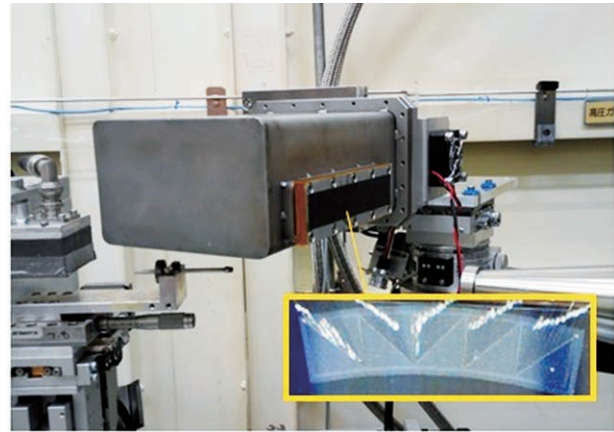


Fig.2 New 5 × 32 channel Si strip detector.

- **High-pressure, high-temperature furnace for supercritical fluids:** This furnace allows us to investigate electron dynamics in supercritical fluid emerging under high-pressure and high temperature condition. We measured plasmon dispersion in Rb up to 14 MPa and 1000 C, where the electron system expanded substantially. We saw the strong damping of the intensity as the density decreases. The project was conducted with collaboration with K. Matsuda at Kyoto University.

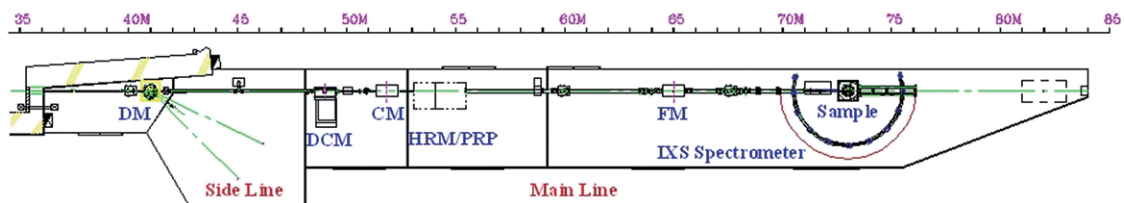


Fig.1 Schematic diagram (top view) of the BL12XU: DM is a diamond monochromator for the sideline, DCM a double crystal monochromator for the mainline, CM a collimating mirror, HRM a high resolution (channel cut) monochromator, PRP a phase retarding plate, FM a focusing mirror, and IXS an inelastic X-ray scattering spectrometer.

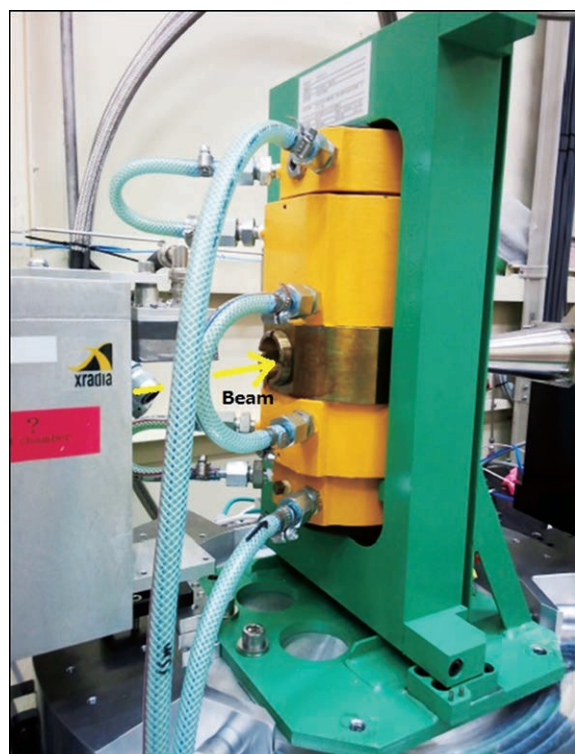


Fig.3 High-pressure furnace for studies on supercritical fluid.

2-2 Experiments

In 2014, we had 10 experiments of non-resonant IXS, 2 of resonant IXS, 1 of non-resonant X-ray emission, 11 of resonant X-ray emission, 3 of high-resolution diffraction. Interesting examples are introduced below.

• High-to-low spin state transition in $\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$

$\text{SrCo}_{0.5}\text{Ru}_{0.5}\text{O}_{3-\delta}$ has oxidation states of 5+ for Ru and 3+ for Co. Co^{3+} ion has a magnetic moment and high-spin state at ambient pressure while converts to low-spin as the pressure increases. The transition was monitored by X-ray emission spectroscopy and becomes completed at 40 GPa, rejecting the possibility of the existence of the intermediate spin state above this pressure as was previously proposed. [J. M. Chen *et al.*, J. Am. Chem. Soc. **136**, 1514 (2014)]

• Pressure induced spin transition revealed by iron M2,3-edge spectroscopy

The L or M edges in transition metals reside in the soft X-ray region. Due to strong absorption cross section of soft X-rays, the high-pressure studies at those edges were lacking although they would include rich information about the valence state or the magnetism. Using a newly built 20 keV spectrometer adopting higher energy X-rays than usual for X-ray Raman scattering, the pressure dependence of the M edge feature was first observed in FeS. [A. Nyrow *et al.*, Appl. Phys Lett. **104**, 262408 (2014)]

3. Sideline

The HAXPES technique is to apply hard X-rays of several keV energy such that the emitted high kinetic energy photoelectrons would have large inelastic mean free path of about 4-10 nm resulting in large contribution from deep inside bulk thus minimize the unavoidable contribution from the surface region in which the electronic structure may be altered from bulk either by lower coordination or by different surface stoichiometry or contamination. The unique design of the sideline HAXPES end station is to have two electron energy analyzers mounted to collect emitted photoelectrons either along the horizontal polarization of incident X-rays or perpendicular to both the polarization vector and the incident beam. The different polarization dependence of atomic orbitals can be used to distinguish the various orbital contributions to the valence bands. For example the *s*-orbitals, which contribute to chemical bonding, would have large cross section of emission along the polarization vector while become almost vanished perpendicular to it, leaving *d*-orbitals, which is responsible for strong electron correlation, the main spectral weight in 3*d* transition metal compounds. These features have been utilized to study temperature and doping dependence of phase transition of various compounds. Core levels on the other hand offer also rich information of the materials. In practice measuring emission along the polarization vector often yield larger count rate for core levels other than *s*-orbitals. Here we provide two examples of these capabilities.

• Understanding the Electronic Structure of IrO_2 Using Hard-X-ray Photoelectron Spectroscopy and Density-Functional Theory

Iridates (Ir^{4+} compounds with $5d^5$ configuration in octahedral local IrO_6 structure) exhibit rich electronic and magnetic properties including both metallic and insulating phases for various compounds. They should behave metallic like in band theory due to odd number of *d*-electrons. It has been identified crystal electric field plus strong spin-orbit coupling (SOC) can explain the insulators as in the Mott insulating phase when the octahedra are nearly perfect. The simple binary IrO_2 compound has the edge sharing quasi-1D octahedral structure as rutile TiO_2 and is metallic. Both valence bands and several core levels are measured by HAXPES and compared to density-functional theory (DFT) to understand why it is metallic. Figure 4 displays the measured valence band spectrum compared to cross section weighted sum of partial density of states (PDOS) from DFT calculation showing good agreement. The features in the valence band denoted II, III, and IV correspond to Ir-O π antibonding, π bonding, and σ bonding orbitals, respectively.

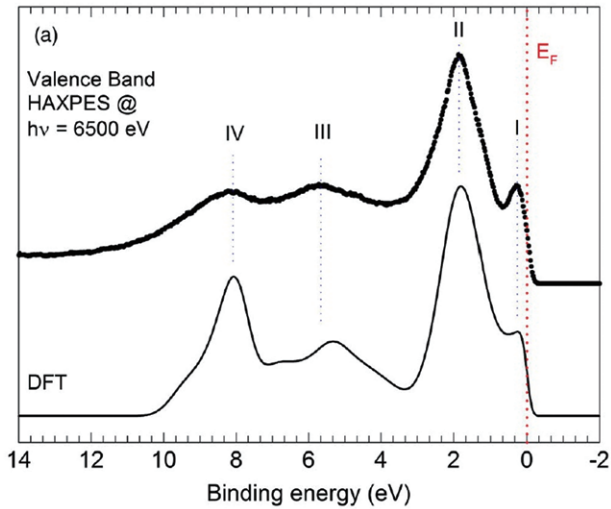


Fig.4 IrO_2 valence band HAXPES spectrum taken by 6.5 keV X-rays. The DFT calculated spectrum is the sum of cross section weighted PDOS. The features denoted II, III, and IV correspond to Ir-O π antibonding, π bonding, and σ bonding orbitals, respectively. Feature I is mainly from Ir t_{2g} orbitals perpendicular to the quasi-1D edge sharing IrO_6 octahedra of the rutile structure.

Feature I is mainly from Ir t_{2g} orbitals perpendicular to the quasi-1D edge sharing IrO_6 octahedra of the rutile structure. Particularly PDOS look very similar with and without SOC because the strong distortion of IrO_6 octahedra causes large overlap of SOC split originally narrow bands rendering SOC effect unimportant to explain its metallic property. [J. M. Kahn *et al.*, Phys. Rev. Lett. **112**, 117601 (2014)]

• Contiguous 3d and 4f Magnetism: Strongly Correlated 3d Electrons in $\text{YbFe}_2\text{Al}_{10}$

Magnetism arises from open shell of a valence localized orbital where its orbital and spin states contribute to a net magnetic moment of an atom or ion and these magnetic moments in a solid interact with one another to form some sorts of short and long range ordering exhibiting magnetism. The 4f orbitals are in principle very localized while a portion of it hybridizes with the mobile conduction bands showing non-integer fluctuating valence state. The 3d orbitals are less localized than the 4f orbitals and both can contribute to the magnetism in $\text{YbFe}_2\text{Al}_{10}$. To understand the rich temperature dependent magnetic properties of this compound it is imperative to know the valence state of Yb. Figure 5 shows the Yb 3d core level spectrum with various contribution of non-magnetic single component Yb^{2+} and magnetic Yb^{3+} with multiplets and their individual plasmon satellites. By comparing to simulation the effective valence state of Yb ions is determined to be 2.38. [P. Khuntia *et al.*, Phys. Rev. Lett. **113**, 216403 (2014)]

* This sideline project is in collaboration with Prof. L. H. Tjeng of the Max-Planck-Institute for Chemical Physics of Solids (MPI-CPfS) in Dresden, Germany.

N. Hiraoka, H. Ishii, Y. F. Liao, Y.-H. Wu and K.-D. Tsuei NSRRC, Taiwan

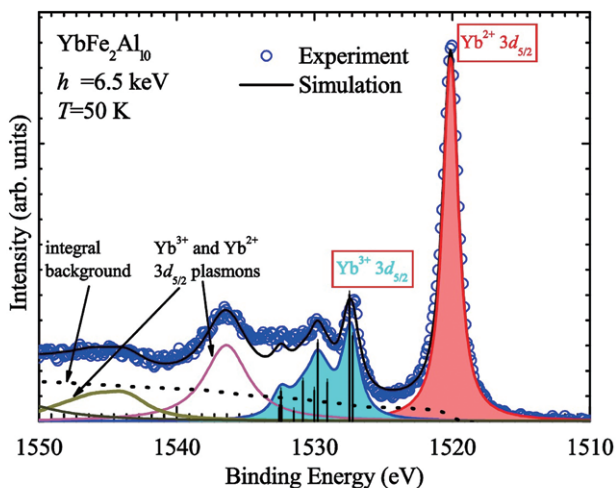


Fig.5 Yb $3d_{5/2}$ core level spectrum of $\text{YbFe}_2\text{Al}_{10}$ taken by bulk sensitive HAXPES at 6.5 keV. The Yb^{3+} exhibit a multiplet structure and is simulated by theory. The 16 eV satellites are due to valence band plasmon excitations from photoelectrons ejected from these core levels and are primarily due to Al contribution. The relative areas under Yb^{3+} and Yb^{2+} peaks accurately yield an effective Yb valence state of 2.38.