BL12XU
NSRRC ID

1. Introduction

BL12XU is one of the two contract beamlines operated by the National Synchrotron Radiation Research Center (NSRRC), Taiwan. It is designed mainly to support inelastic X-ray scattering (IXS) experiments and hard X-ray photoemission spectroscopy (HAXPES). BL12XU has an undulator light source, and two branches: the mainline and sideline (Fig. 1). The mainline, which has been fully operational since 2001, is used by both domestic and international scientists for IXS. The sideline is used for HAXPES. The HAXPES end-station is opened to general users, although some adjustments and upgrades by the Max-Planck Institute for Chemical Physics of Solids (MPI-CPfS) are ongoing.

2. Instrumentation

The following instrumental development occurred in FY2019. Larger upgrades on the inelastic spectrometers are planned for the next few years.

2-1. High energy-resolution fluorescence–detected (HERFD) XAS on 4d transition metal compounds

High energy-resolution fluorescence–detected (HERFD)-XAS is a promising technique to investigate the chemical status of specific ions during a reaction. This technique is attracting increased attention from chemists as the lifetime broadening can be suppressed, realizing high-resolution spectra. This advantage is especially useful for 4*d* transition metals such as Pd or Ag, which typically have lifetime broadenings as large as 5–10 eV. However, such experiments are challenging because few X-ray spectrometers are applicable to high-energy (15–25 keV) fluorescence from 4*d* transition metals.

To resolve this issue, a Laue-type X-ray Raman spectrometer is utilized in HERFD-XAS for Zr, Nb, Mo, Ru, and Pd standard foils. Figure 2 shows the results. Features hidden due to lifetime broadening in normal XAS are clearly visible in HERFD-XAS. This experimental configuration will be applied to more functional materials such as electrocatalysts, including Ag, Pd, or other 4*d* transition metals.

3. Experiments

In FY2019, 24 experiments were conducted using resonant IXS (RIXS), 8 of non-resonant IXS

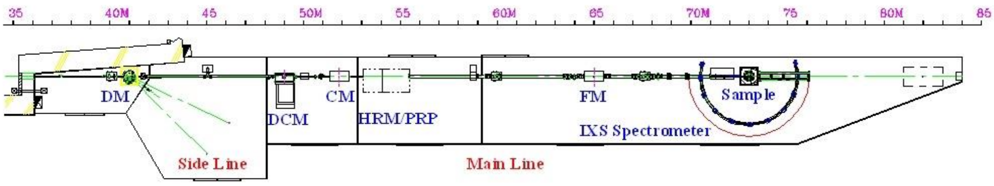

Fig. 1. Schematic diagram (top view) of the BL12XU. DM is a diamond monochromator for the sideline, DCM a double crystal monochromator for the mainline, CM a collimating mirror, HRM a high resolution (channel cut) monochromator, PRP a phase retarding plate, FM a focusing mirror, and IXS an inelastic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

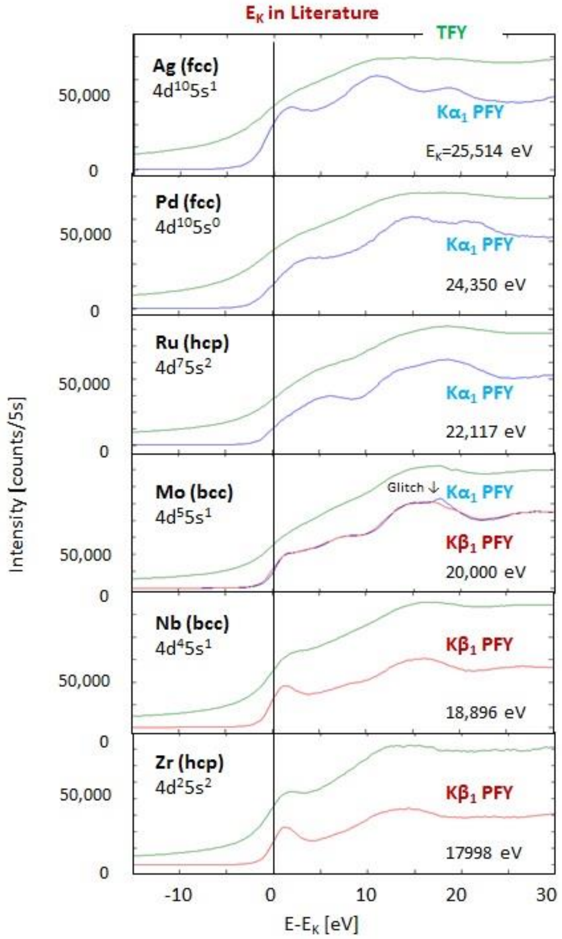

Fig. 2. HERFD-XAS spectra on standard foils for 4*d* transition metals. HERFD spectra are represented by PFY (partial fluorescence yield), while normal-XAS is represented by TFY (total fluorescence yield).

(NIXS), and 21 of HAXPES. Representative examples are introduced below.

3-1. Electronic structure of dense solid oxygen from insulator to metal investigated with X-ray Raman scattering

High-pressure XAS on low-Z element samples is extremely difficult or almost impossible using conventional XAS techniques. This is because the absorption edges are in the VUV or soft X-ray regions, where photons are strongly absorbed in a pressure cell before reaching and after exiting the sample. Such edges can be measured by inelastic scattering.

Fukui et al. studied the insulator-to-metal transition in O_2 at very high pressures, up to 130 GPa, by X-ray Raman scattering. Solid oxygen, which is stable at high pressures > 6 GPa, undergoes several structure transitions as the pressure increases and eventually transits to the metallic phase around 100 GPa. Peaks due to the π* and σ* bands were observed around 532 eV and 542 eV in X-ray Raman spectra, respectively. As the pressure increased, the peak positions increased on the energy axis, but abruptly decreased around 100 GPa. This indicates an energy lowering related to the insulator-to-metal transition. Moreover, a weak shoulder feature was observed on the tail of the π* peak before the transition, which may indicate the existence of a hidden phase transition such as an insulator-to-semimetal transition or an antiferromagnet-to-nonmagnet transition [1].

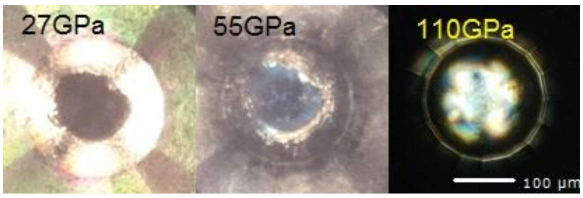

Fig. 3. Solid oxygen compressed in a diamond anvil cell. At ~100 GPa, oxygen undergoes an insulator-to-metal transition.

3-2. Interplay of atomic interactions in the intermetallic semiconductor Be_5Pt

Semiconducting substances form one of the most important families of functional materials. However, semiconductors containing only metals are very rare, and the chemical mechanisms behind their ground-state properties are only partially understood. Amon et al. investigated the intermetallic compound Be_5Pt using HAXPES. Unexpectedly, the HAXPES spectra revealed a semiconducting behavior (bandgap of 190 meV) for Be_5Pt. It also showed two kinds of Be ions, which existed in different environments in the crystal and provided evidence of strong charge transfers from Be ions at both sites to the Pt ion. In fact, the combination of relativistic effects and the charge transfer due to the electronegativity difference between the components controlled the semiconducting behavior [2].

N. Hiraoka*, Y.F. Liao, H. Ishii, M. Yoshimura, and K.D. Tsuei
National Synchrotron Radiation Research Center

References:

[1] Fukui et al, Proc. Nat. Acad. Soc. 116, 21385 (2019)
[2] Amon et al., Angew. Chem. Int. Ed. 58, 15928 (2019)