

BL12XU NSRRC ID

1. Overview

BL12XU is one of the two contact beamlines between National Synchrotron Radiation Research Center (NSRRC, Taiwan), Japan Synchrotron Radiation Research Institute (JASRI) and RIKEN SPring-8 Center. 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 coupled with a pulsed laser, were also carried out. The sideline 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 20 keV IXS spectrometer, and high resolution IXS optics. Also, we made a design of a high-pressure, high temperature furnace for IXS studies on supercritical fluid. The following is a short description of the high-resolution optics.

- **25 meV NIXS setup:** We measured nitrogen gas with the highest energy resolution that we achieved. The Si 800 channel-cut monochromator provides 10 meV band width at 9.9 keV while a spectrometer consisting of a Si 555 spherical analyzer and a home-built Si strip detector of a 125-micrometer spatial resolution, allowing to achieve an overall resolution 25 meV. The beautiful energy resolved peaks due to various vibronic modes of nitrogen molecules were observed (see Fig.2). [Yi-Geng Peng *et al.* Phys. Rev. A **89**, 014502 (2014)].

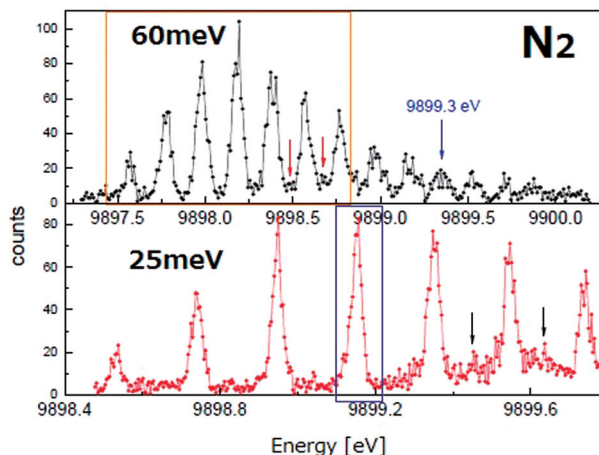


Fig. 2 Vibronic excitation features in N_2 gas, measured by 25 meV resolution setup.

2-2 Experiments

In 2013, we carried out 6 experiments of non-resonant IXS, 5 of resonant IXS, 2 of non-resonant x-ray emission, 11 of resonant x-ray emission, 3 of high-resolution diffraction, and 1 of coherent diffractive imaging. Interesting examples are introduced below.

- **Molecular-to-polymer transition in CO_2 observed by NIXS:** Solid CO_2 is known to have various crystal structures as a function of temperature and pressure. Below 30 GPa, they are all classified as molecular solids, characterized by weak bonds between molecules. However strong inter-molecular interaction rapidly develops above 30 GPa and the molecular solids become polymers. We observed a crossover of two phases: Raman features near the carbon and oxygen *K*-edges show transitions of strong π^* and σ^* excitations indicative of sp^2 hybridization in molecular form at low pressures, to a weakening of π^* while

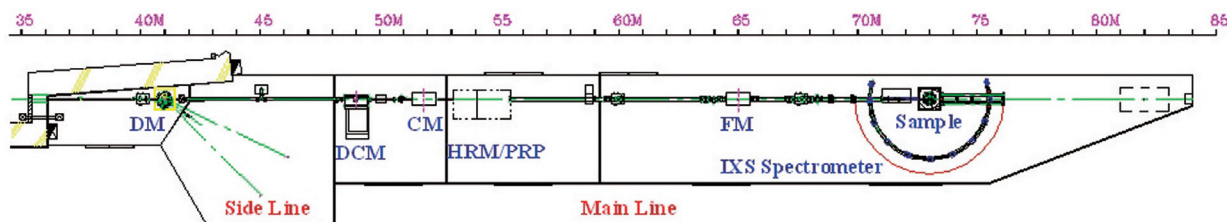


Fig. 1 Schematic diagram (top view) of the BL12XU: DM is a diamond monochromator for the sideline, DCM a double crystal monochromator for the mainline, CM a collimating mirror, HRM a high resolution (channel cut) monochromator, PRP a phase retarding plate, FM a focusing mirror, and IXS an inelastic x-ray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

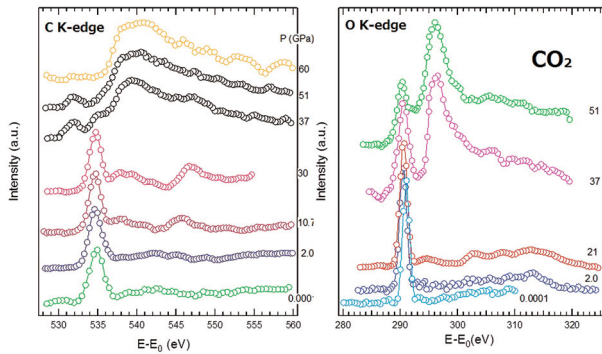


Fig. 3 Carbon and oxygen *K*-edge features in solid CO₂ as a function of pressure.

enhancement of σ^* excitations indicative of forming sp^3 bonds in polymer form above 37 GPa (see Fig.3). [Shieh *et al.*, Proc. Nat. Aca. Sci. **110** 18402 (2013)].

• **Valence transition in rare-earth monochalcogenides under pressure:**

Rare-earth monochalcogenides, RE-X, where RE = Sm or Yb while X = S, Se, or Te, generally shows a valence instability between 2+ and 3+ of the RE charge states associated with their localized 4*f* electrons. The valence states were determined by PFY-XAS at the *L*₃-edges as a function of pressure. Sm compounds showed a dramatic change of a valence state from ~2+ to ~2.8+ while Yb compounds a relatively smaller change from ~2+ to ~2.3+. A unified model describing those behaviors was proposed. [Jarrige *et al.* Phys. Rev. B. **87**, 115107 (2013)]

3. Sideline

The design concept of the sideline HAXPES end station is to explore the (linear) polarization dependence on the photoelectron emission anisotropy of various angular momentum components in valence bands of strongly correlated materials, and from it to extract the (temperature dependent for example) behavior associated with only the components responsible for electron correlation. We built a new end station in 2012 incorporated with two analyzers arranged to measure emitted electrons either parallel to the (horizontal linear) polarization direction or perpendicular to it and the (horizontal) photon beam. It is known in the hard X-ray range that the asymmetry parameter beta of atomic photoionization cross section is very near 2, thus the photoemission of an *s*-state in the perpendicular direction should be completely suppressed. However, we found much more intense emissions of both O 1*s* core level and the Ni 4*s* component in the valence bands in the perpendicular geometry in NiO including finite angular acceptance of analyzers. Fig. 4(a) shows the O 1*s* emission intensities normalized to Ni 2*p* on these two geometries. An unphysically large angular acceptance would be required to explain the experimental data. Similarly

unexpectedly large Ni 4*s* components appear in the valence bands as shown in Fig. 4(b). These results indicate some appreciable side-scattering processes are still taking place in solids even though it is believed that forward-scattering dominates at these high kinetic energies.

* 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.

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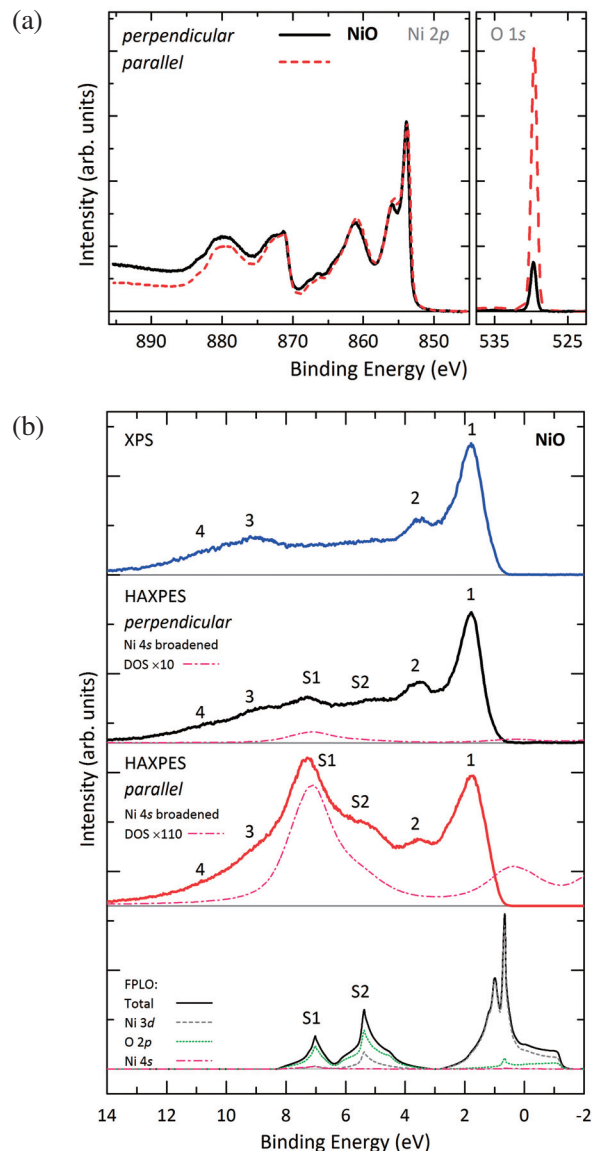


Fig. 4 (a) Polarization dependent photoemission intensities at 6.5 keV photon energy for Ni 2*p* and O 1*s* in NiO, the latter is normalized to the former; and (b) the valence bands data compared to element and angular momentum decomposed partial DOS from an LDA calculation. Both core and valence data show unexpectedly large intensities from the *s*-components.