Hard X-ray emission spectroscopy with pink beam

K. O. Kvashnina, A. Rossberg, J. Exner, A. C. Scheinost

Valence-band X-ray emission spectroscopy (XES) with a "pink beam", i. e. a beam with large energy bandwidth produced by a double-multilayer monochromator, is introduced here to overcome the weak count rate of monochromatic beams produced by conventional double-crystal monochromators. Our results demonstrate that – in spite of the large bandwidth in the order of 100 eV – the high spectral resolution of the Johann-type spectrometer is maintained, while the two orders of magnitude higher flux greatly reduces the required counting time. The short working distance Johann-type X-ray emission spectrometer and multilayer monochromator is available at ROBL.

XES is an element-selective method which provides a unique approach to study the electronic structure. The element sensitivity is achieved by creating a core hole with incident X-rays above the X-ray absorption edge. The event, when the core hole is filled by the valence electrons, can be measured by XES. Due to the dipole-allowed selection rules, XES can be used as fingerprint of the partially occupied density of states projected onto a selected atom in hybridization with ligands. Thus, the effects of the crystal structure and hybridization between different atoms and their electronic states can be studied by XES.[1, 2]

EXPERIMENTAL. Measurements of the non-resonant $K\beta_{1,3}$ XES lines of the transition metals are commonly fast even with monochromatic beam, but the valence band $K\beta_{2,5}$ XES lines are very weak (Fig. 1), hence, require very long counting times. In order to overcome this limitation related to the weak count rate, we used a double-reflection multilayer monochromator at ROBL. Multilayer optics operate at a typical incident angles of a few degrees with a bandwidth about 100 times larger than that of the conventional double-crystal optics. At the same time, the multilayer optics provides a significant flux increase, which is commonly used for methods such as X-ray imaging or fluorescence spectroscopy, where the narrow bandwidth of the crystal optics is not required. We show here that combination of the multilayer optics with X-ray emission spectrometer gives the possibility to probe the valence band excitations of the matter near the Fermi level in a relatively short time while maintaining a high energy resolution.

RESULTS. Figure 1 compares the $K\beta_{2,5}$ XES lines of ZnO recorded with either the Si(111) double-crystal (red) or the double multilayer (blue) monochromator. A 0.5-m bending-radius Johann-type X-ray emission spectrometer is used for both measurements.[3] Under these conditions, we gained a factor of 25 in the data collection rate with multilayers compared to crystals. The time spent on the $K\beta_{2,5}$ XES data collection with multilayer optics is 15 minutes (blue curve, Fig. 1), which compares to 1.5 hours with the Si(111) crystals (red curve, Fig. 1).
Therefore, the spectrometer equipped with a 0.5-m crystal analyzer in combination with the pink beam improves the signal's intensity by a factor > 100 in comparison to the 1-m spectrometer in combination with a monochromatic beam. The proposed method is broadly applicable to time-resolved X-ray emission analysis at different generations of synchrotron facilities and X-ray free-electron laser light sources.

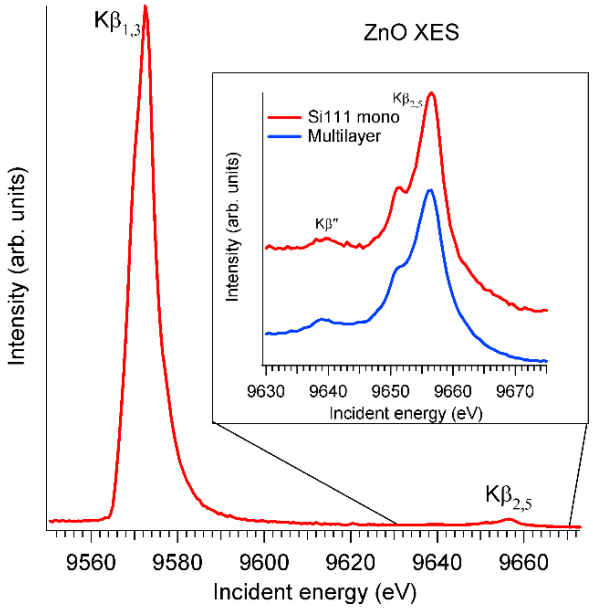

Fig. 1: Experimental $K\beta_{1,3}$ and $K\beta_{2,5}$ emission lines of ZnO recorded with a pair of Si(111) crystals and the 1-m spectrometer (red), and with a pair of multilayer s and the 0.5 m spectrometer (blue).

[1] Kowalska, J. K. (2016) *Inorg. Chem.* **55**, 4485–4497.
[2] March, A. M. (2015) *J. Phys. Chem. C* **119**, 14571–14578.
[3] Kvashnina, K. O. *et al.* (2016) *J. Synch. Radiat.* **23**, 836–841.