

Hard X-ray Photoelectron Spectroscopy: New Opportunities for Chemical and Physical Analysis

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Photoelectron spectroscopy (PES) is a well established technique in condensed matter research and is also widely used to study the chemical composition of matter and the valences of ions [1,2]. A sample hit by monochromatic light of energy $h\nu$ emits electrons whose kinetic energy E_{kin} is related to its binding energy E_{bin} by Einstein's famous equation $E_{\text{kin}} = h\nu - E_{\text{bin}} - \phi$ (ϕ is the work function of the material). Measuring the energy distribution of the emitted electrons then yields an image of the density of states of the sample. Typical light sources used in such experiments are UV gas discharge lamps (UV Photoelectron Spectroscopy, UPS) and X-ray sources with energies of 1256 eV (Mg K_{α} radiation) or 1486 eV (Al K_{α} radiation). The latter is known as XPS (X-ray Photoelectron Spectroscopy) or ESCA (Electron Spectroscopy for Chemical Analysis). However, the significance of these spectra is limited since they strongly depend on the properties of the surface. Having a probing depth of 5 Å – 15 Å (for UPS and XPS, depending on the material) means that only the surface of a sample is probed. The surface, however, may have very different properties than the bulk. On the one hand, it might be oxidized or have adsorbed contaminations from the environment. In this case, meaningful spectra can only be obtained by carefully preparing the sample surface under ultra high vacuum (UHV) conditions and removing any adsorbates. On the other hand, even a perfectly clean surface – especially of strongly correlated materials – may have different properties than the bulk since the different environment can cause changes in the electronic structure.

In recent years progress in instrumentation and especially the availability of high energy synchrotron radiation for generation of intense hard X-rays with unprecedented energy resolution opened up new possibilities for photoelectron spectroscopy and thus for condensed matter research and chemical analysis. It is now possible to do HArD X-ray PhotoElectron Spectroscopy (HAXPES) measurements with photoelectrons with an energy range of 6 keV – 12 keV, and count rates and resolution

comparable to those of standard XPS/ESCA machines. The key advantage of using high energy photons is that also the photoelectrons have much higher kinetic energy and thus an increased inelastic mean free path [3]. Depending on the material probing depths of 50 Å – 200 Å are possible, i.e. ten times larger than in UPS or XPS/ESCA.

This allows to record high quality spectra of samples even if their surface is not atomically clean. Careful surface preparation is no longer mandatory (though sometimes still favourable). For systems which exhibit different properties at the surface, the bulk can be probed directly with this technique. Furthermore, it is possible to measure high temperature phases of oxides which is problematic with UPS or XPS techniques because of oxygen loss at the surface.

As an example, Figure 1 shows the valence band spectrum of a silver film grown on a MgO substrate. This spectrum was taken using a photon energy of 7.6 keV. The sample was measured without any *in situ* treatment after being in air for long time. Despite the sample surface being covered with atoms and molecules adsorbed from air, the spectrum has the typical lineshape of silver valence band. Thus, the probing depth of this technique is indeed large enough to avoid sizeable surface contributions to the spectra.

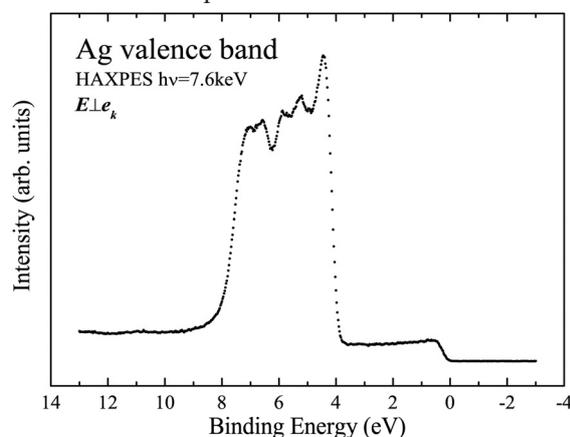


Fig. 1: HAXPES valence band spectrum of a silver film grown on an MgO substrate, measured using 7.6 keV photon energy. The sample surface was not treated before the measurement.

The photoionization cross sections in the hard X-ray regime are very low. This is why very bright synchrotron radiation is needed. Moreover – and this is very crucial for our experiment – also the relative weights of the cross sections for the different orbitals (i.e. s , p , d , etc.) change at high photon energies, which is demonstrated in the following example.

Figure 2 (a) shows the valence band spectrum of a ZnO single crystal taken with a photon energy of 1486 eV (XPS). The valence band spectrum is essentially composed of the Zn $3d$ states at binding energy around 10 eV – 12 eV and the O $2p$ states around 4 eV – 9 eV. The excitation spectra of this compound are well understood and a simulation of the valence band spectrum using LDA+ U band structure calculations agrees very well with the experimental data. Note that the contribution of the Zn $4s$ spectral weight is small in this case.

The same spectrum collected in a HAXPES experiment (7.6 keV photon energy) using a typical horizontal geometry, has a very different lineshape (Fig. 2 (b)). In this geometry the detected photoelectrons are emitted in the direction parallel to the polarization vector (E) of the incoming light. Using the bandstructure calculations the change in spectral weight can be assigned to a much increased contribution of the Zn $4s$ orbital. And, indeed, this change can be explained by a relative increase of the photoionization cross section of the s orbitals compared to the p and d orbitals when going to higher photon energies [4–6]. By identifying the properties of the $4s$ states it is possible to study the chemical bonding which, in this compound, exists between the Zn $4s$ and the O $2p$.

The spectrum in Figure 2 (c) was measured under the same conditions, but with vertical experimental geometry where the detected photoelectrons are emitted perpendicular to the direction of the polarization of the light. It is different from (b) and, surprisingly, much more similar to the XPS. To explain this feature, the so-called asymmetry parameter β in the angle – dependent differential photoionization cross section (Fig. 3) needs to be taken into account. For s electrons β is close to 2 [4–6]. As it can be seen in Figure 3, this causes a strong enhancement of the s spectral weight for an $E \parallel e_k$ geometry and an almost complete suppression for $E \perp e_k$ (γ being the angle between E and e_k and e_k being the wave vector of the photo electrons). By choosing the experimental geometry one can quasi switch the sensitivity to s electrons.

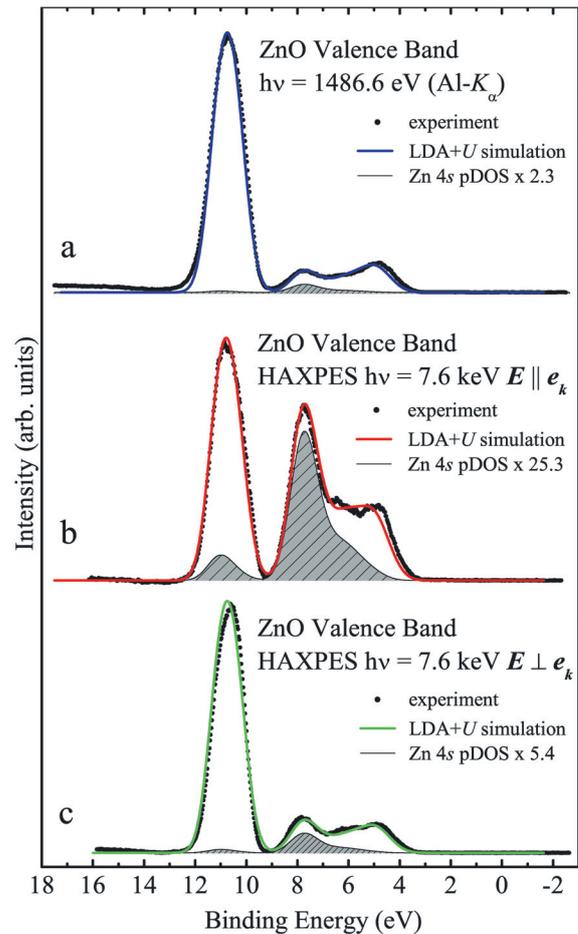


Fig. 2: Photoelectron spectra of a ZnO single crystal, taken with a photon energy of (a) 1486 eV ($Al K\alpha$), (b) and (c) 7.6 keV. For (b), electrons emitted with wave vector e_k parallel to the polarization of the light were recorded, for (c): electrons perpendicular to the polarization of the light. Note the different spectral weights of the Zn $4s$ states depending on photon energy and geometry.

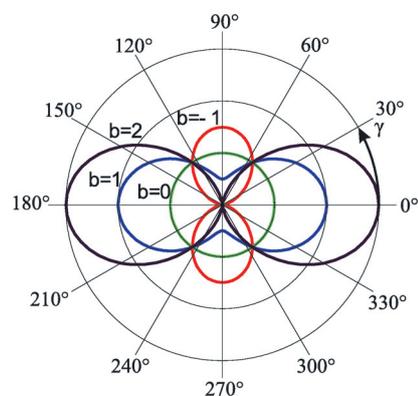


Fig. 3: Polar plot of the angular dependence of the differential photoionization cross sections for various values of the asymmetry parameter in the range $-1 \leq \beta \leq 2$.

Our experimental work is performed at the SPring-8 synchrotron radiation facility in Hyogo, Japan. A sideline of Beamline BL12XU (Taiwan Beamline) is dedicated to the joint HAXPES project of MPI CPFS and NSRRC. Close to the undulator the beam is split and monochromatized by Bragg scattering from a diamond crystal (Fig. 4). Further sections of the sideline are mounted on a movable platform allowing to use a photon energy range from 6 keV to 12 keV (according to the Bragg's law). To improve the resolution, the light is guided through a silicon channel cut monochromator. A K-B mirror system focuses the beam to the center of the measurement chamber. The light spot has a footprint of $50\ \mu\text{m} \times 50\ \mu\text{m}$. As for any hard X-ray experiment, the whole beamline and experimental stage is placed in a lead hutch to shield any harmful radiation.

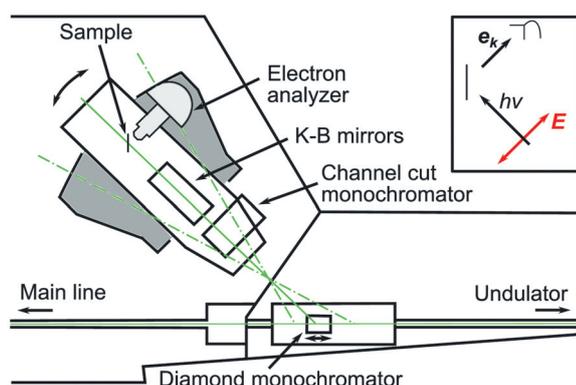


Fig. 4: Top view sketch of the BL12XU (Taiwan Beamline) sideline dedicated to HAXPES at SPring-8. The inset shows the vectors E and e_k (both in the paper plane) for the horizontal setup.

The spectrometer consists of a system of UHV chambers. The main component is the electron energy analyzer A-1HE from *MB Scientific*. Samples are mounted on an $xyz\theta$ manipulation stage which is – as well as the table on which the whole setup is placed – fully motorized to allow the tuning of the sample position while the beam is on. A flow cryostat is used to cool the sample with liquid nitrogen or liquid helium. The cooling setup is complemented with a heating stage on the same arm. A temperature range of 10 K–750 K can be covered without changing the setup. A separate preparation chamber is used for sample transfer and storage and for *in situ* cleaving.

In order to make use of the polarization dependence of the photoionization cross section as described above, the whole system can be installed in two geometries, i.e. with horizontally or vertically mounted analyzer (Fig. 5). Currently, a change in the geometry involves a complete reconstruction of the setup. A major redesign is planned to avoid the need for this demanding procedure. The experiment will be equipped with a second electron analyzer. With two analyzers mounted perpendicular with respect to each other and to the beam, it will be possible to switch swiftly between s sensitive and s non-sensitive measurements, or possibly to measure in both modes simultaneously. This will make the instrument unique in the world.

To conclude, the strongly increased probing depth of HAXPES allows to study the electronic structure and to do chemical analysis of a wide range of materials without the need for extensive *in situ* surface treatment and cleaning. It is now possible

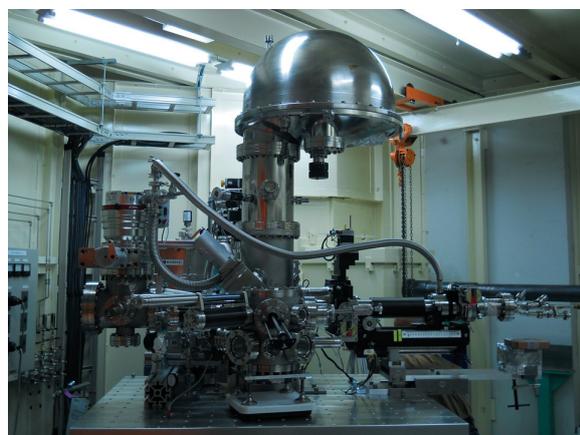
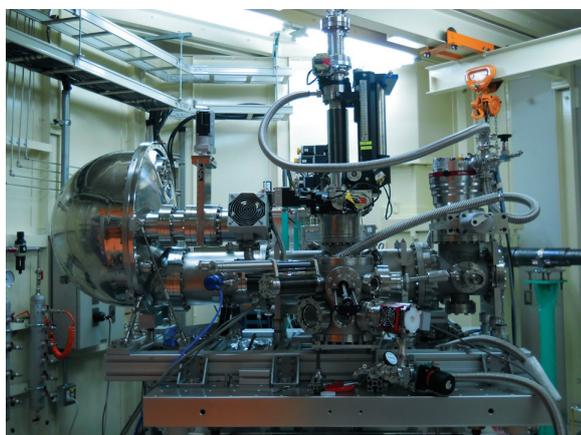


Fig. 5: Photographs of the experimental setup with the electron analyzer oriented horizontally (left) and vertically (right), respectively, thus making use of the geometry dependence of the photoionization cross sections of the different orbitals. (Photon beam is coming from the rear into the chamber, polarization vector horizontal.)

to study buried interfaces as well as powder samples using this technique. The polarization dependence of the spectra allows to investigate the nature of the chemical bonding, in particular the role of *s* orbitals. For strongly correlated systems in which *d* and *f* states are important, the perpendicular geometry can be used to obtain spectra which are free from *s* electron contributions.

For the near future it is planned to work on several projects, partly in collaboration with other sections of MPI CPfS: the study of electronic structure of intermetallic compounds, of high temperature phases of transition metal oxides and of materials with high oxidation states.

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