

## Application Note

# Probing bulk band structure using ARPES

Traditionally, angular resolved photoemission (ARPES) is used to study the band structure of materials. The photon range used normally makes the technique surface sensitive. In order to increase the bulk sensitivity of the technique, ARPES spectra could be acquired using higher excitation energies. As the energies are increased the demands of the analyser, in terms of energy and angular resolution, is increasing. In this application note we present data from Chuck Fadley and co-workers, recorded using VG Scienta hemispherical analysers, showing band structure for > 1keV kinetic energies and true hard x-ray (HAX) angular resolved spectra at 6 KeV: data that have revolutionized the method of ARPES as it now allows probing the true bulk band character of a material.

The probing depth of photoelectron spectroscopy (PES) is dependent upon the mean free path ( $\mu$ ) of the electrons. Between 10 and 2000 eV the mean free path is only of the order of a few Å up to 10 or 20 Å, with its minimum escape depths around 50 eV (Hüfner, Photoelectron spectroscopy 3rd, Springer, 2003). For higher energies the probing depth could be described having the approximate relation of  $0.85\sqrt{E_k}$ ,  $E_k$  being the kinetic energy. Thus, for electrons of 4-6 keV  $E_k$  the probed depths are up to 10 nm, being of a bulk character (K. Kobayashi, NIMA 601 (2009) 32), see Fig. 1.

ARPES is one of the most powerful techniques to study band structure of solids and surfaces. In ARPES the intensity of the spectral features is measured with respect to  $E_k$  and angle ( $\theta$ ). The angular coordinates can then be transferred into  $k_{||}$ -space ( $k_{||}$ ) according to  $k_{||} = 0.512\sqrt{E_k}\sin(\theta)$ . For energies, up to about 100-150 eV the transition can be regarded as direct, as the initial state wave vector ( $k_i$ ) can only make a transition to a final state with wave vector ( $k_f$ ) according to  $k_f = k_i + g_n$ , where  $g_n$  is a reciprocal lattice vector. But for higher energies the momentum of the photon ( $k_{hv}$ ) also has to be accounted for ( $k_f = k_i + g_n + k_{hv}$ ) and the spectral features have to be shifted with respect to the measured emission angle.

More important: at higher energies (around 1 keV) the phonon broadening of the spectra and the angular averaging in the spectrometer leads to what is known as the x-ray photoelectron spectroscopy (XPS) limit. This is where the spectra represent the matrix-element weighted density of states (DOS) of the crystal and the origin of the intensity change with angle is dominated by diffraction effects (as seen

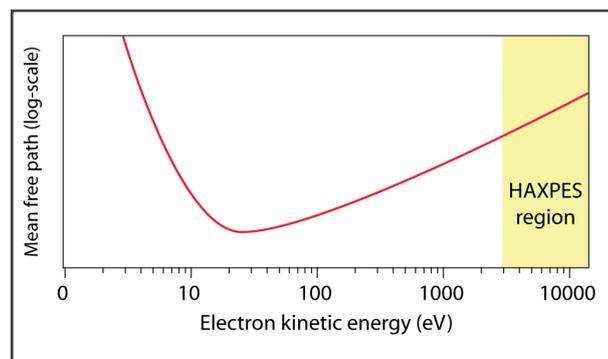


Figure 1: Schematic illustration of the electron mean free path as a function of kinetic energy.

in x-ray photoelectron diffraction (XPD) experiments). The phonon broadening of the spectra is temperature dependent and can approximately be described by a temperature Debye-Waller factor, which describes the fraction of direct transitions remaining for different temperatures. The temperature dependence of this effect is used by Fadley and co-workers to acquire band structure measurements using high excitation energy, in order to probe the bulk states of the crystal under study. If spectra are measured at different temperatures either DOS/XPD (high temperature) or band structure features (low temperature) are dominating the spectra. A data set consisting of low and high temperature spectra could then be used to normalize the spectra such that the spectral contribution is dominated by the band dispersion features, as done by Bostwick and Rotenberg, and described in PRB 84(2011)045433. (see Fig. 2).

The data in Fig. 2 were recorded with the Multi-Technique Spectrometer/Diffractometer at the Lawrence Berkeley National Laboratory; this is a custom-designed system equipped with a SES200 hemispherical analyser upgraded to SES2002 standard and a non-monochromized Mg K  $\alpha$  x-ray source. Even if the spot size is very large the combined spatial and angular resolution of the setup is determined to be

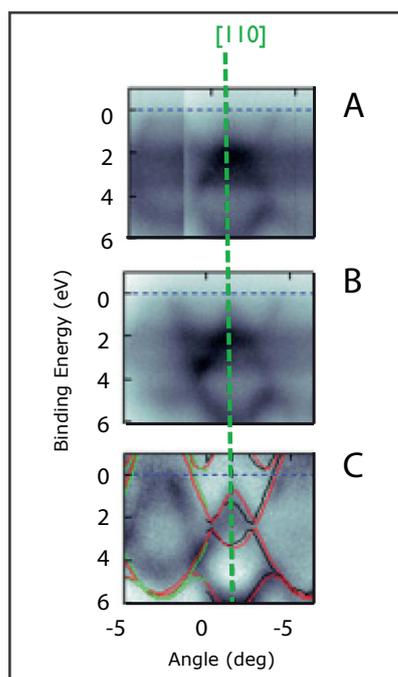


Figure 2: Data of W(110) recorded at A) room temperature and B) liquid nitrogen temperature using an excitation energy of 1253.6 eV (non-monochromized Mg K  $\alpha$  x-ray source). C) Normalized data, where the DOS and XPD effects are accounted for. The data is compared to theory (solid lines). (At PRB 84(2011)045433 data is displayed over a broader interval of -5 and 40 degrees).

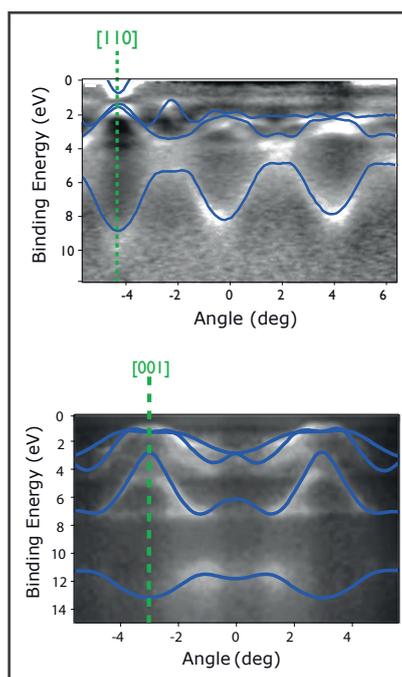


Figure 3: Normalized Data of W(110) after room temperature and 30 K normalization (see Gray et al. Nature Materials, 10 (2011) 759). Excitation energy of 5956 eV (synchrotron radiation). [110] direction of crystal marked with green dashed line. The data is compared to theory (solid lines).

below 1 degree and sufficient to resolve the angular dependence of the sample, as seen in Fig. 2 for the case of W(110).

Beyond this, a similar system has been used to demonstrate the possibility to record ARPES using multi-keV energies, and to perform true hard x-ray angular resolved photoemission (HARPES), for W(110) at 5956 eV and GaAs(001) at 3238 eV (See Gray et al. Nature Materials, 10 (2011) 759). The experiments were performed at the synchrotron radiation facility SPring-8, in Hyogo, Japan, using the undulator beamline BL15XU equipped with a Scienta Omicron R4000 high energy hemispherical analyser, the overall energy resolution (monochromator plus analyser) was set to 250 meV and the angular resolution was about 0.25-0.30 degrees.

These experiments show the possibility of measuring ARPES at >1 KeV using both in-laboratory

and synchrotron sources. The most crucial effect to overcome is the phonon-induced broadening, and a method to reduce this effect via cryo-cooling is shown in the articles by Fadley and co-workers. More generally the phonon broadening could be estimated from the Debye-Waller factors. Papp et al. states in PRB 84(2011) 045433 that it is possible to measure band structure if about 50% of the transitions show a direct transition behaviour and that the Debye-Waller factors then has to be below 0.5 at a temperature of 20 K, which is an achievable temperature for many cryo-cooled sample holders. It should therefore be possible to record ARPES for many materials in the 1-3 keV range and for other materials it is even possible to perform measurements up to the 5<sup>-10</sup> keV regime. An additional limitation is the so-called recoil effect, which affects the energy position and resolution. But Papp et al. state

that it should be possible to study many elements at up to about 4keV if not higher. These are all in all promising predictions for the new field of HARPES.

This application note is written in collaboration with Prof. Chuck Fadley, Department of Physics, University of California, Davis, and Materials Sciences Division, Lawrence Berkeley National Laboratory, USA. It is based on the C.S. Fadley, Journal of Electron Spectroscopy and Related Phenomena, 178-179(2010) 2; C.S. Fadley, Nuclear instruments and Methods in physics research A, 601 (2009) 8; A.X. Gray et al. Nature Materials, 10 (2011) 759; and C. Papp et al. Physical review B 84 (2011) 045433.

**How to contact us for further info:**

[www.ScientaOmicron.com](http://www.ScientaOmicron.com)  
[info@ScientaOmicron.com](mailto:info@ScientaOmicron.com)

