Band mapping in higher-energy X-ray photoemission

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We have studied the temperature dependence of W(110) soft x-ray angle-resolved photoemission spectra between 300K and 780K. The temperature dependence of the data can be analyzed qualitatively in terms of a direct-transition band-dispersion regime ("UPS" limit) versus a non-direct-transition density-of-states regime ("XPS" limit). We also discuss the implications of this work for future experiments on other materials and at even higher photon energies up to 10 keV.

There is growing interest in extending valence electronic studies with angle-resolved photoemission (often referred to as "band mapping", but more correctly viewed as quasiparticle spectra) into the soft x-ray, and even hard x-ray, regimes. Such measurements take advantage of the greater photoelectron information depths at higher kinetic energies, thus probing more accurately bulk, rather than surface, electronic structure. Furthermore, three-dimensional, rather than two-dimensional, band structure and Fermi surfaces may be studied by going to higher photon energies. In comparison to low-energy band mapping, however, additional effects must be taken into account in both carrying out such measurements and in interpreting data. These include the increased angular resolution required to probe a small enough region in the Brillouin zone (BZ), the need to allow for the photon momentum in wave-vector conservation, and thermal effects due to phonon creation and annihilation during photoexcitation that smear out the specification of the initial wave vector. It is useful in this discussion to think in terms of two limiting regimes: very low energies and/or temperatures in which band mapping is possible via direct or k-conserving transition (DTs)–the so-called UPS limit, and high energies and/or temperatures in which emission is fully averaged over the BZ to yield density-of-states (DOS) sensitivity–the XPS limit.

Our measurements (see [1] for details) were carried out on a (110)-oriented tungsten crystal at beamline 4.0.2 of the Advanced Light Source in Berkeley, using the Multi-Technique Spectrometer/Diffractometer located there. The exciting synchrotron radiation was p-polarized and the angle between photon incidence and electron exit was fixed at 70°. The sample orientation was adjusted after allowing for photon momentum so as to as nearly as possible sample points along the Γ-to-N line in the BZ. A Scienta electron spectrometer with SES2002 performance was used

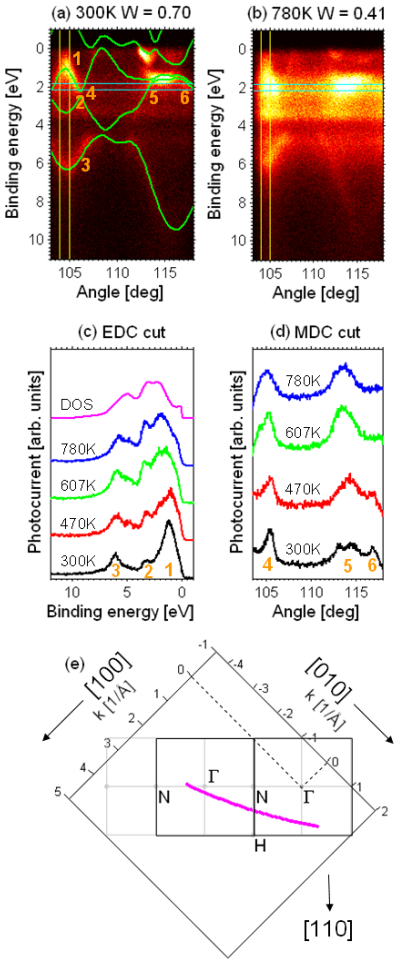

FIG. 1: (a)-(b) Plots of intensity versus angle of emission for hν = 870 eV. In (a) also the transitions allowed with free-electron final states are shown. (c) The temperature dependence of energy distribution curves integrated over 20 channels in angle as indicated in (a) and (b). A comparison to the W density of states (DOS), as broadened by experimental resolution of 150 meV is also shown in the topmost curve. (d) The temperature dependence of momentum distribution curves at one selected energy, again as indicated in (a) and (b). (e) The average locus of points in the BZ sampled in this data, assuming direct transitions and free-electron final states.

to accumulate angle-resolved spectra with a standard 2D detection scheme, the average angular resolution was approximately 0.5°.

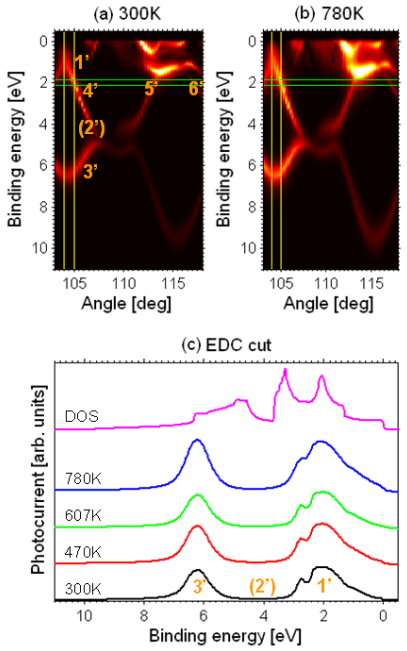

FIG. 2: As Fig. 1, but for one-step photoemission calculations including temperature effects via complex phase shifts. See text for details.

We have analyzed the data in first approximation by requiring wave-vector conservation according to $\vec{k}_f = \vec{k}_i + \vec{g}_{hkl} + \vec{k}_{h\nu}$ where the $\vec{k}$-conservation condition has been modified to allow for the non-negligible photon momentum at higher excitation energies, by assuming free-electron final states for which the energy inside the solid is $E_f(\vec{k}_f) = \hbar^2 k_f^2/2m_e = E_{kin} - V_0$, where m_e is the mass of the electron, E_{kin} is the kinetic energy outside the surface, V_0 is the inner potential of 15 eV, and by using initial state energies from a band structure calculated using the WIEN2k code [4].

The novel aspects of this work are in measuring detailed two-dimensional plots of binding energy vs. wave vector as a function of temperature, with prior work on tungsten only considering selected single directions of emission and lower energy and angular resolution [2]. Furthermore, we compare the experimental data with state-of-the-art one-step photoemission theory [3] which includes a precise evaluation of matrix element effects and an attempt to include phonon effects, while prior work used only simple direct-transition theory together with free-electron final states and a qualitative/semi-quantitative estimate of the fraction of DTs via suitable Debye-Waller (DW) factors [2] with these being calculated from: $W(T) = \exp[-\frac{1}{3} g_{hkl}^2 \langle U^2(T) \rangle]$ where g_{hkl} is the magnitude of the bulk reciprocal lattice vector involved in the direct transitions at a given photon energy and $\langle U^2(T) \rangle$ is the three-dimensional mean-squared vibrational displacement.

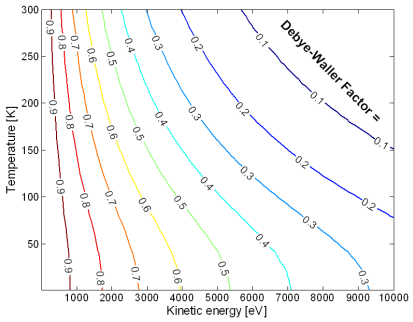

FIG. 3: Debye-Waller factors for valence-band photoemission from W at various temperatures over 0-300K and electron kinetic energies over 0-10 keV. These permit a rough estimate of the fraction of transitions yielding simple band mapping features.

Figures 1 and 2 show experimental and theoretical photoemission data presented both as two-dimensional maps and energy distribution curve (EDC) and momentum distribution curve (MDC) cuts. From Fig. 1(a) the agreement between the experiment and free-electron theory is very good, which proves that band mapping is indeed possible at 870 eV, an energy higher than used in most prior ARPES work. Similarly comparison between Figs. 1(a) and 2(a) is favorable. However, by comparing Figs. 1(c) and 2(c), it is clear that theory in which phonon effects are incorporated only via complex phase shifts is not found to reproduce the smearing of the spectral features at the higher temperature, and this indicates that a more accurate approach in which phonon creation and annihilation are taken into account in the photoemission process is needed to adequately describe such data.

Finally, we consider what might be expected if the photon energy is taken to much higher values up to 10 keV, again for the example case of tungsten. At this point, we can only make use of the DW factors to estimate the fraction of transitions that are direct, and a family of curves for different temperatures over 0-300K and electron kinetic energies over 0-10 keV are shown in Fig. 3. From these curves, it is clear that, if we use the rough criterion of at least 50% direct transitions, then at least for W, one can work at 300K with photon energies up to about 1.7 keV, and with cooling to 4 K, with photon energies up to about 5.4 keV.

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