Hard X-ray photoemission with angular resolution and standing-wave excitation

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Several aspects of hard X-ray photoemission that make use of angular resolution and/or standing-wave excitation are discussed. These include hard X-ray angle-resolved photoemission (HARPS) from valence levels, which has the capability of determining bulk electronic structure in a momentum-resolved way; hard X-ray photoelectron diffraction (HXPD), which shows promise for studying element-specific bulk atomic structure, including dopant site occupations; and standing wave studies of the composition and chemical states of buried layers and interfaces. Beyond this, standing wave photoemission can be used to derive element-specific densities of states. Some recent examples relevant to all of these aspects are discussed.

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1. Introduction

I will in this overview discuss two different aspects of hard X-ray photoemission (HXPS, HAXPS) that enhance its ability to characterize a broad range of materials systems:

- measurements on single crystal or epitaxial systems in which angular resolution is important, including both valence-level hard X-ray angle-resolved photoemission (HARPS) and the closely related core-level hard X-ray photoelectron diffraction (HXPD),
- experiments on nanoscale layered materials in which a multilayer mirror or crystal Bragg reflection is used to create a standing-wave in the sample such that depth resolution can be significantly enhanced and buried layers and interfaces can be studied or element-resolved densities of states determined, respectively.

2. Hard X-ray angle-resolved photoemission

2.1. Introduction

Traditional angle-resolved photoemission (ARPES) with excitation in the ca. 20–150 eV range has clearly evolved to be the technique of choice for studying the electronic structure of surfaces and complex new strongly correlated and magnetic materials. Efforts are also underway to use even lower excitation sources below 10 eV, with the aim of both increasing energy and momentum resolution and for some systems also increasing bulk, rather than surface, sensitivity. With these advances, and the development of brighter variable-polarization and femtosecond-scale light sources, together with improved spectrometers making use of time-of-flight and next-generation detectors, e.g. for spin detection, there is thus no doubt that ARPES will continue to be a leading tool of materials physics.

However, it is clear from prior experimental and theoretical work that ARPES with excitation up to 150 eV or so remains a very surface sensitive probe, thus necessitating careful in situ sample cleaning, cleaving, or even synthesis to avoid the measurement of surface-associated artifacts. A key measure of this surface sensitivity is the electron inelastic mean free path (IMFP \( \lambda_e \)), which roughly measures the mean depth of electron emission without inelastic scattering, and both experimental [1,2] and theoretical [3] IMFP studies showing that the only reliable way to increase bulk or buried layer and interface sensitivity for all material types is to go to higher photon energies in the soft X-ray (ca. 0.5–2 keV) or hard X-ray (ca. 2–5 keV) regime. I will here focus on the hard X-ray regime, operationally defined from 2 keV upward, as 2 keV is roughly the point at which Bragg-reflection crystal monochromators begin to be used instead of gratings.

For this reason, interest has grown in carrying out ARPES studies with photon energies above 500 eV [4], and going into the multi-keV range [5]. As one limiting factor in such higher-energy measurements, it has been known for some time that the \( \vec{k} \)-conserving direct-transition (DT) effects that are critical to ARPES...
can be smeared out by phonon effects, even though they could be observed in some systems up to 1.5 keV [6]. Several more recent studies have explored the systematics of such measurements as a function of photon energy, temperature, and polarization for some simple test materials [5,7–9]. However, it is only very recently, that it has been pointed out by Gray et al. that ARPES can be carried out in the multi-keV hard X-ray range (HARPES), and in fact going up to 6 keV for W as a test case [5].

2.2. Basic considerations

Let us now consider some of the advantages, disadvantages, and special considerations in using HARPES and then turn to the few first examples of its applications.

• **Greater probing depth:** As already noted, a key advantage is in being able to probe more deeply in the sample, with the expectation that IMFPs should increase roughly as [kinetic energy]^{0.75}.

  An additional benefit of this greater probing depth is that the smearing in momentum perpendicular to the surface \( \overline{p}_n \sim h k_{\perp} \), which will be given approximately via an uncertainty principle argument by \( \Delta k_{\perp} \approx \frac{1}{2} \overline{A}_e \) should decrease with increasing energy. Thus, truly three-dimensional band mapping becomes more possible at higher energies.

• **Allowance for photon momentum:** It has long been recognized that there will be deviations from the dipole approximation in ARPES carried out at 1 keV or more [6], such that the usual form of the \( \hat{k} \)-conservation equation for direct transitions from \( k_i \) to \( k_f \) has to be modified to allow for the photon momentum via \( k_i = k_f + \hat{t} k_{\perp} \), where \( k_{\perp} = 2 \pi v/c \) is the photon wave vector and \( \hat{t} k_{\perp} \) is the relevant reciprocal lattice vector. In convenient units, this is \( k_{\perp} \) (in Angstroms\(^{-1}\)) = 0.000507 (Photon energy in eV). For a given experimental geometry, this correction is easily made. Some relative magnitudes as compared to the Brillouin zone (BZ) of tungsten are illustrated in Fig. 1 for soft and hard X-ray excitation.

• **Phonon and recoil effects:** It has also long been known that the creation and annihilation of phonons during photoemission can effectively smear out the specification of \( k_i \) [6,10], leading finally in the limit of high energy and high temperature to a matrix-element weighted density-of-states (MEWDOS) or XPS limit, in which valence-electron intensities exhibit also core-like X-ray photoelectron diffraction (XPD) effects [11–13]. As a rough guide to the degree of direct-transition behavior expected in an ARPES experiment, one can use a temperature-dependent Debye–Waller factor \( W(T) \) calculated for the relevant \( \overline{g}_n \), which roughly represents the fraction of direct transitions [6,10,14]. This factor can be calculated from \( W(T) = \exp(-g^2 u^2(T)>/2) \), with \( u^2(T) > \) the one-dimensional mean-squared vibrational displacement at temperature \( T \). This immediately suggests the use of cryogenic cooling of the sample.

  Intimately linked to phonon effects is the fact that momentum and energy conservation must allow for the photoelectron momentum, which ceases to be negligible on going into the multi-keV range. In a worst-case scenario, a single atom of mass \( M \) recoils as the photoelectron leaves, and in this case the energy lost to the photoelectron is given by \( E_{\text{rec}} \approx (k^2 + k_f^2)/2M \approx 5.5 \times 10^{-4}(E_{\text{kin}}(\text{eV}))/M(\text{amu}) \). Roughly speaking, the fraction of transitions in which the entire lattice can be thought to recoil, effectively making \( M \) infinite and the recoil energy zero, is the Debye–Waller factor, in the same spirit as the recoil–free fraction in Mössbauer spectroscopy. Several studies have explored recoil effects on core and valence level spectra, particularly by Takata et al. and Suga et al., including the energy broadening associated with them [15,16].

  As a comprehensive but approximate guide to these photon and recoil effects, Fig. 2 shows calculated \( W(T) \) contours at 20 K and for a value of 0.50 that might be considered a minimum for doing realistic ARPES as a function of average atomic weight \( M \) and Debye temperature [14]. We will see below that this criterion appears to be conservative for some cases, thus permitting HARPES at higher energies and/or temperatures than might be expected. The additional curves showing recoil energies make it clear that, relative to the current ultimate resolutions of ~50 meV in HARPES, these effects should be negligible in the soft X-ray regime <2 keV, but will become important for lighter atoms in the multi-keV range.

• **The free-electron final state:** A convenient aspect of soft- and hard-X-ray ARPES is that the final state for energies above about 500 eV to
can in many respects be approximated as a free-electron, with energy \( E(k) = p_f^2 / 2m_e = h^2 k_f^2 / 2m_e \), where \( p_f \) is the photoelectron momentum and \( m_e \) is the electron mass, as illustrated below in some recent analyses of experimental data [6,9,14].

- Levels of theoretical interpretation and modeling: To date, there are basically three levels of theoretical interpretation and modeling:
  1. Simply looking at the final state as a free electron in an extended-zone scheme, translating it into the first BZ via \( k_f = k_i - k_{in} - g_{in} \), and asking qualitatively where it cuts the ground-state band structure.
  2. More rigorously requiring \( k \)-conservation and computing the locus of points in energy and \( k_i \) that satisfy it, in order to localize \( k_f \) in the BZ more precisely [6,9,14].
  3. At the highest level, carrying out full one-step photoemission calculations that include the surface and all matrix element effects, so as to be able to accurately represent intensities [5,9,17]. In particular, I will show below results obtained by Minar, Braun, and Ebert based on a time-reversed low-energy electron diffraction (LEED) final-state approach, as computed in a spin-polarized relativistic Korringa–Kohn–Rostoker framework [17].

- Complementary core- and valence-level spectroscopy: Having such high photon energies also means being able to access core levels from all of the atoms in a sample, including e.g. the O and surface C that are often present as constituents or surface impurities, as well as deeper core levels in any atom, and making use of chemical shifts, multiplets, satellites, and other fine structure in these spectra as an adjunct to the ARPES spectra. Measuring at room temperature also yields valence-level density-of-states related information. Such core- and valence-level spectra have been very productively used in prior HXPS [18–23] and HARPES studies [5,24] by our group and its collaborators.

2.3. Some first proof-of-principle and application studies

\( W \) and GaAs–true hard X-ray ARPES: Figs. 3 and 4 now illustrate truly hard X-ray ARPES as measured for the first time by Gray et al. [5] at SPring-8 for two separate cases: \( W(110) \) with 5.9 keV excitation and GaAs(100) with 3.2 keV excitation, both at 300 K and 30 K. The energy resolution was here \( \approx 250 \) meV and the angular resolution \( \approx 0.3^\circ \). Fig. 2 is highlighted for these two materials, and one expects to be able to go up to about 5–6 keV for \( W \) with a negligible 18 meV recoil shift, and to be able to go to about 2–3 keV for GaAs with again a negligible 10 meV recoil shift. Figs. 3(i), (ii) and 4(i), (ii) show the experimental geometry and the expected region sampled in \( k \)-space for \( W \) and GaAs, respectively. Figs. 3(iii) and 4(iii) show a succession of experimental and theoretical HARPES images.

For \( W \), one expects on the basis of Fig. 3(ii) to sample points in \( k \)-space along \( \ldots \Gamma-N-\Gamma \ldots \). Looking now at the actual results, Fig. 3(iii)(a) shows data obtained at 300 K, for which \( W \approx 0.09 \), a situation expected to yield the XPS limit with both MEWDOS and XPD features showing. Indeed, no dispersive features are seen, and the modulations at any angle are found to closely resemble the \( W \) MEWDOS, as shown by the yellow curve at right, which is integrated over angle. In Fig. 3(iii)(b) are shown results after cooling to 30 K, for which \( W \approx 0.45 \), and approximately half the intensity is thus expected to be involved with direct transitions. For this case, dispersive features clearly appear, although they are still superposed with MEWDOS features, as expected. In addition, in both of these raw data panels, the MEWDOS-like intensity exhibits modulations with angle that can be as much as 30%. These are shown as a gray curve in Fig. 3(iii)(a), and are simply hard X-ray photoelectron diffraction effects, as has been seen before with soft X-ray excitation of valence bands for cases in the XPS limit [11–13]. Thus, both dispersive band effects and XPD effects can be seen in the same dataset, with relative amounts depending on temperature and photon energy.

In Fig. 3(iii)(c), the raw low-temperature image has been corrected with a two-step procedure that involves dividing by the detector window average over energy (to approximately correct for XPD effects) and by the window average over angle (to approximately correct for MEWDOS effects) [25]. The dispersive features are much more evident in this corrected image, and suggest this as a general procedure for correcting images that should be useful for many systems. The green curves superposed on the corrected
Fig. 3. Hard X-ray ARPES (HARPES) from W(110) at room temperature and 30 K, with a photon energy of 6 keV: (i) the experimental geometry. (ii) the extended-zone picture. (iii) (a) The room temperature data, with energy-integrated XPD curve and angle-integrated matrix-element-weighted DOS (MEWDOS) curve. (b) The 30 K data, showing a mix of MEWDOS and ARPES dispersive features. (c) The data corrected for XPD and MEWDOS [25], with the green curves representing free-electron final-state simulations allowing for a small sample tilt. (d) One-step photoemission calculations, with no tilt included.

From Ref. [5].

Fig. 4. HARPES from GaAs(100) at room temperature and 30 K, with a photon energy of 3.2 keV: (i) The experimental geometry. (ii) The extended-zone picture. (iii) (a) The room temperature data, with energy-integrated XPD curve and angle-integrated MEWDOS curve. (b) The 30 K data, showing a mix of MEWDOS and ARPES dispersive features. (c) The data corrected for XPD and MEWDOS [25], with the green curves representing free-electron final-state simulations. (d) One-step photoemission calculations. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

From Ref. [5].
experimental results in Fig. 3(iii)(c) are based on free-electron final state modeling at level [2], which, with the inclusion of a slight sample tilt from a fully symmetric geometry, shows excellent agreement as to the positions of most features. Finally, in Fig. 3(iii)(d) are shown one-step calculations at level [3], which are able to predict the experimental intensities very well over −2 to −6 degrees, although by not yet being able to incorporate the sample tilt, these results are more symmetric over the full angle range than is seen in experiment.

Fig. 4 shows a completely analogous set of results from GaAs(100), with similar conclusions for each of the panels. Here, one expects the ARPES detector image to sample points in k-space along ...X–Γ–X... In Fig. 4(iii)(a), with a value of W = 0.01 at 300 K, the MEWDOS-like results (yellow curve) and the XPD-like results (dark blue curve) are again evident. In Fig. 4(iii)(b), the uncorrected experimental data already shows significant dispersive bands, really beyond what one would expect for the W value of 0.31 that is relevant. This is a first sign that the criteria embodied in Fig. 2 may be too conservative for some cases. Again in Fig. 4(iii)(c), after the same two-step correction as in Fig. 3(iii)(c), the free-electron final-state calculations agree well with experiment as to the positions of all major features. However, one difference here is that the deep-lying more localized and largely As 4s band at ~12 eV does not show the weak dispersion expected, but rather exhibits more XPD-like modulation, as expected for a core level.

The results of Figs. 3 and 4 thus clearly indicate that it should be possible to carry out more bulk-sensitive electronic structure studies at much higher photon energies than have been typically employed in the past. In addition, for GaAs, bands have been resolved with a lower W value of 0.35, so the estimates in Fig. 3(a) prove to be too conservative, such that higher energies in the few-keV range will likely being usable for many systems. It is also expected that better procedures for correcting for the phonon-associated MEWDOS-like features will be developed, along with better microscopic theoretical treatments of such phonon effects.

Fig. 5. Survey spectrum from Ga$_{0.97}$Mn$_{0.03}$As(001), again with 3.2 keV, and with enlarged insets from scanning longer on Mn 2p and Mn 3s. From Ref. [24].

Fig. 6. Comparison of one-step theoretical [(a) and (b)] and corrected experimental [(c) and (d)] ARPES results for GaAs and Ga$_{0.97}$Mn$_{0.03}$As, respectively, again at 30 K and with 3.2 keV excitation. Panels (e) and (f) show the core-like As 4s band, with HXPD effects. Note the shift in the mirror-symmetry positions near 3 degrees between the VB results and the XPD due to the photon wave vector. From Ref. [24].
From Ref. [24].

(to be discussed below [28]), thus extending the energy range even further.

Ga$_{1-x}$Mn$_x$As—a first application of HARPEPS: I will now briefly discuss a first application of HARPEPS to the elucidation of the electronic structure of a material over which some controversy has existed: the dilute magnetic semiconductor (DMS) Ga$_{1-x}$Mn$_x$As, with $x \approx 0.03–0.06$. The key question here is the nature of the Mn-induced states, and whether they represent a narrow impurity band that is separated cleanly from the GaAs p valence bands, or whether these states are merged with the GaAs impurity bands. In the former case, the so-called double-exchange mechanism would be active in producing ferromagnetism and in the latter, it would be what is referred to as p–d exchange. Gray et al. [24] have studied a sample with composition Ga$_{0.37}$Mn$_{0.03}$As, again at Spring-8 with 3.2 keV photon energy and in the same experimental system as Figs. 3 and 4. In Fig. 5, a survey spectrum from this study is shown, and the advantage of having core-level spectra is immediately evident, in that the Mn 2p spectrum shows a sharp screening satellite that is only observed with more bulk-sensitive hard X-ray excitation [26], and which has in a further HXPS study by Fujii et al. [21] provided information on the relative importance of such screening between the bulk and the surface of such DMS materials. Also seen in this spectrum is the Mn 3s multiplet splitting, whose 5.4 eV magnitude in fact suggests a Mn$^{3+}$ 3d$^5$ state rather than the Mn$^{2+}$ 3d$^6$ that is usually assumed in this material [27]; perhaps this is due to final-state screening that affects one member of the multiplet more than another so as to decrease the splitting. A final point concerning this spectrum is that, even at the very low 3% dopant level present here, it is possible to resolve these subtle core-level fine structure effects. It is thus easy to predict that dopant levels on the scale of 1% should be capable of such core-level structure in the future, and we discuss below an example of a so-called “delta-doped” SrTiO$_3$ sample that is in this category.

In Fig. 6, the HARPEPS data from GaAs and GaMnAs are compared, with one-step theory shown in (a) and (b), similarly corrected experiment in (c) and (d), and the 12-eV core-like band again exhibiting XPD in (e) and (f), respectively. The intensity distributions of the GaMnAs are in all panels smeared out relative to those in GaAs, as might be expected from the presence of the Mn atoms which disturb the long-range periodicity. One-step theory is in agreement with experiment in predicting these differences, with other theoretical results being presented elsewhere [24].

Fig. 7 now shows a comparison of angle-integrated experimental data for GaAs and GaMnAs ((a) and blowup of the difference in (c)) and angle-integrated one-step theory ((b) and (d) and again blowup of difference in (d)). There is striking agreement here in the changes induced by Mn, including almost all of the features seen in the difference curves. These results indicate an impurity band (1 in experiment, 1’ in theory) at about 400 meV below the Fermi energy, but additional changes through the entire GaAs valence-band region. Further analysis of the k-resolved results very near $E_F$ [24] permit concluding that we must for this material consider both p–d exchange and double exchange, or really a fully covalent mixed model, to explain its ferromagnetism.

This study thus represents a first application of HARPEPS to a complex system whose electronic structure was in debate, and it suggests other such opportunities in the future.

2.4. More accurate modeling of phonon effects in HARPEPS

In a prior soft X-ray study of ARPS from W(110) at 870 eV, the effects of phonons on data obtained as a function of temperature have been measured [9], and a recent development in the one-step theoretical approach that includes vibrational atomic displacements via the coherent potential approximation has been
Combining HARPES with standing-wave excitation for studies of multilayer structures, as discussed in Section 4 below, should also permit depth- and k-resolved measurements of electronic structure.

Limitations which should be kept in mind for such studies are that the energy resolutions for the near future will probably not be better overall than ~50 meV, and are more typically in the 100–200 meV range, and that the spectrometer angular resolutions in k-space can limit the exact specification of positions in the BZ, esp. for systems with larger spatial unit cell dimensions (and thus smaller BZ dimensions) than the examples shown above: W with a = 3.16 Å, and a BZ size of ~1.99 Å⁻¹, and GaAs with a = 5.65 Å, and a BZ size of ~1.11 Å⁻¹. With regard to angular resolution, it is however fortuitous that the longer k vector at higher energies implies that only a smaller angular range needs to be measured to span a few BZs, thus making the job easier for the electron optical system involved, and offering the promise of angular resolutions down from the present ~0.2° [5] to perhaps as low as 0.02° in the future. In fact, a spectrometer in the author’s laboratory is already operating at 0.04° resolution over 2–4.5 keV (cf. Fig. 1). Finally, phonon smearing of k specification will always be present to some degree, with this suggesting that lower photon energies be preferred [2]. Finally, it should be recognized that ARPES can be carried out over the full continuum of excitation energies, with soft X-ray ARPES (SARPES) in the few hundred to 2 keV regime also recently emerging as a powerful and diverse tool for studying electronic structure that is also more bulk sensitive than traditional ARPS at lower energies and that can inherently achieve better energy and BZ-position resolutions than those of HARPES [29]. Combining SARPES and HARPES on the same system is thus a particularly attractive prospect for the future.

3. Hard X-ray photoelectron diffraction

3.1. Introduction and basic considerations

XPD we have already seen as part of the HARPES data presented, but one also has to ask how XPD will change on going into the HXPD regime, as addressed in a theoretical study by Winkelman et al. [30] Fig. 9 illustrates this, by means of both a standard XPD pattern obtained at 964 eV [31] in (a), and a succession of theoretical simulations that span 0.5–20 keV. The theory here involves noting that, as the IMP increases with energy, the diffraction process expands from the local-order cluster picture that is illustrated in Fig. 10(a), and which has been used in several computer programs for simulating XPD previously (as for example, the EDAC code [32]), to a process in which Bragg reflection from planes and resultant Kikuchi-band formation represent a more efficient calculation method. Although in fact, the cluster approach yields a good description of the 964 eV data [30,31], it is also clear that the Kikuchi band (or dynamical diffraction) simulation shown in Fig. 9(b) at 1 keV is in excellent agreement with experiment. As energy increases, the cluster size needed to accurately describe the Bragg reflections, as well as the increasing number of partial waves required to accurately model the scattering, render the cluster approach more and more time consuming. It is thus clear that modeling HXPD in the multi-keV regime in the future should involve expanded use of dynamical-diffraction/Kikuchi-band modeling.

3.2. Application to dopant sites in crystals

As one illustration of what might be learned from such HXPD data, Fig. 11 shows Kikuchi-band simulations of emission of a photoelectron at 6 keV from (a) a lattice site in a Si(111) crystal and

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Fig. 8. One-step theoretical calculations of HARPES for emission along W(110) at 6.4 keV, with the red curves showing the angle-resolved prediction at 10 K and 300 K, and the constant-form blue curve representing an angle-averaged prediction that should very closely resemble the density-of-states, as weighted by different matrix elements. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

From Ref. [28].

shown by Minar et al. to accurately describe the development of MEWLOS-like features as temperature is raised [28,29].

More relevant to the present paper is work by the same group on W(110) at 6.4 keV [28], which is summarized in Fig. 8. Here, only theory is shown, with the blue curves being angle-integrated HARPES results, which should represent in first approximation a matrix-element weighted DOS, and the red curves representing HARPES spectra for emission along [1 1 0] as temperature is increased from 10 K to 300 K. At the low temperature, there is a clear k-resolved HARPES feature at a binding energy of about 4.0 eV. The known band structure of W indicates that this is due to selective sampling near the N point in the BZ, as also expected from Fig. 9(b). But beyond this, there is a clear convergence of HARPES theory to the angle-integrated curve, and in fact, the spectrum for 300 K is in remarkably close agreement with the yellow MEWLOS curve at right in Fig. 3(iii)(a). Taken together, these soft and hard X-ray results suggest that phonon effects in ARPES can for the first time be modeled correctly, which of course also means that more accurate information concerning electronic structure can be extracted from the data at all energies and temperatures.

2.5. Hard X-ray angle-resolved photoemission–future directions and limitations

In conclusion, HARPES at >2 keV should have broad applications to studying the electronic structure of complex bulk materials, including multilayer nanostructures composed of them. Additional aspects that will certainly be exploited in the future are variable polarization to emphasize different orbital components, as well as to study magnetic order via circular or linear dichroism; and spin-resolved studies to directly study magnetic electronic structure.
Fig. 9. (a) Experimental XPD pattern of C 1s emission from diamond at 964 eV. (b) Calculated XPD and HXPD patterns for various energies from 0.5 to 20 keV. The calculations were done using the Kikuchi-band/dynamical diffraction method.
From Refs. [30,31].

As a related recent example of a study of doped material, although not in fact involving HXPD, Kaiser et al. [34] have applied HXPS at 5 keV using Petra III to a delta-doped SrTiO3 layer that consisted of a 3-nm thickness of 6% La-doped SrTiO3 embedded in a SrTiO3 film, with a 4.5-nm thick capping layer of undoped SrTiO3 (see Fig. 12(a)). In Fig. 12(b), survey spectra are compared for the delta-doped sample (blue curve) and for a thick uniform sample of the same dopant concentration (red curve). Although La 3d intensity is clearly seen in the thick reference, it requires longer counting to see it in the delta-doped sample, but the inset

Fig. 10. Comparison of the two models used for interpreting photoelectron diffraction: (a) the short-range order cluster picture that is most useful for lower energies below ca. 1 keV and (b) the Kikuchi-band or dynamical diffraction picture that is more appropriate for multi-keV energies.
From Ref. [30].
Fig. 11. Calculated photoelectron diffraction pattern for a Si(1 1 1) surface at 6 keV photoelectron kinetic energy from dopants randomly distributed in the Si lattice. (a) Impurity located at the substitutional (Si) sites; (b) impurity located at the tetrahedral interstitial (T) sites.

From Ref. [30].

Fig. 12. (a) Sample configuration for a 3.0 nm La_{0.06}Sr_{0.94}TiO_3 delta-doped layer embedded in undoped SrTiO_3 with a 4.5 nm capping layer of SrTiO_3. (b) Survey spectra obtained with a photon energy of 4990 eV and covering a range of 0–950 eV binding energy from the delta-doped layer of (a) (blue curve) and from a thick 30 nm La-doped STO film with the same La concentration (red curve). The spectra have been offset vertically for clarity. The inset shows an amplified version of the La 3d region obtained at two different energies. (c) Ti 2p spectra, again compared for the delta layer and a thick doped reference. (d) As (c), but for the valence-band region. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of the article.)

From Ref. [34].

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in (b) demonstrates that this is possible, including the well-known screened and unscreened peaks for both La $3d_{3/2}$ and $3d_{5/2}$, which are found to be identical in both the delta layer and the thick sample. More importantly, the presence of Ti$^{3+}$ in the delta layer is evident as a shoulder in the blue curve of Ti 2p spectra in Fig. 12(c), which again compares delta layer to thick reference. Finally, Fig. 12(d) shows an increase in the density of states near the Fermi level for the delta layer that is consistent with separate conductivity measurements. Thus, even with the strongly attenuating SrTiO$_3$ overlayer, the influence of the La in both core-level and valence-level spectra could be studied, suggesting fruitful study of low-level dopant effects in the future, together with HXPD measurements to further determine site types in such highly epitaxial systems.

3.3. Hard X-ray photoelectron diffraction: future directions and limitations

HXPD thus should become a useful tool for structure studies in bulk systems with complex composition, with the only requirement being that the measurements be done with sufficiently high angular resolution, which one can estimate from Figs. 9 and 11 to be on the order of 0.2$^\circ$. However, as noted above, these resolutions are presently achievable in HARPES measurements [5], and so should not be a significant limitation. Varying polarization in such measurements should also be useful, with circular dichroism in fact arising from both non-magnetic [35] and magnetic [36] origins. One additional aspect of HXPD that might be exploited is to study its temperature dependence, as an adjunct measurement to temperature dependence in HARPES, in an attempt to more quantitatively allow for phonon effects in both types of data, with very little data of this type available at this time [37]. Finally, from a theoretical point of view, expanding the existing bulk-oriented Kikuchi band/dynamical diffraction methodology [30] to explicitly include the precise nature of the photoelectron excitation via the differential photoelectric cross section and the presence of the surface will be necessary for arriving at a fully quantitative and versatile description of HXPD.

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4. Hard X-ray photoemission with standing-wave excitation

4.1. Introduction

As the photon wavelength $\lambda_x$ (in Å) $= 12.398$/[(photon energy in eV) decreases to the few nm scale at around 400 eV, it is also possible to begin to make use of strong reflectivity from multilayer samples or substrates with this periodicity to create an X-ray standing wave that can in turn be scanned vertically through the sample in a controlled way so as to yield much enhanced depth resolution. Similarly, as the photon wavelength reaches interplanar distances in single crystals at around 2 keV, Bragg reflections can similarly create strong standing waves that have been used to deconvolve valence-band spectra into their element-specific contributions [38,39]. I will here focus primarily on work by my group and its collaborators on nm-scale standing waves associated with synthetic multilayer structures, but will also comment on some most interesting single-crystal Bragg studies by other groups briefly.

4.2. Basic considerations

As illustrated in Fig. 13, there are three ways in which the standing-wave field can be selectively moved perpendicular to the reflecting layers in a multilayer: by scanning the angle over the Bragg angle, thus generating a rocking curve, by fixing the incidence at the Bragg angle and varying the photon energy, and by scanning a focused X-ray spot incident at the Bragg angle along a sample with one layer in a wedge profile. In the case of scanning the incidence angle $\theta_{inc}$, the relevant equation for the standing-wave intensity at a given point is $I(\theta_{inc}) \propto 1 + R(\theta_{inc}) + 2 \sqrt{R(\theta_{inc}) \cos(\phi(\theta_{inc}) - 2\pi P)}$, where $R$ is the reflectivity, $f$ is the so-called coherent fraction of the sample that is associated with a Bragg reflection, $\phi$ is the X-ray optical phase difference between incident and reflected waves, and $P$ is the positional phase at the point in space at which the intensity is evaluated (in units of $\lambda_x$). In an optimal situation, this intensity can thus vary by $\pm 2 \sqrt{R}$ as indicated in Fig. 13. A similar formula holds for scanning photon energy, with $I$, $R$, and $\phi$ then functions of $h\nu$: In any such experiment with Bragg reflection, the period of the standing wave intensity will be very nearly equal to the period of the reflecting planes. The multilayer-based photoemission techniques have thus far been primarily developed in the soft X-ray regime, and have been reviewed in detail elsewhere [40–42], so I will thus focus here only on a few recent studies involving hard X-rays. Quantitative analysis of such standing-wave data requires considering the detailed reflection, transmission, and absorption of the radiation at each interface and within each layer of the sample, as well as the anisotropic excitation of photoelectrons at each depth and their propagation to the surface and escape from it, for which Yang et al. have written a software package that is reviewed elsewhere [43].

4.3. Some representative applications

$SrTiO_3/La_{0.7}Sr_{0.3}MnO_3$-interface-resolved core- and valence-level spectroscopy: In a recent standing-wave photoemission study of a multilayer composed of alternating 4 unit cells of the band insulator SrTiO$_3$ and 4 unit cells of the half-metallic ferromagnet La$_{0.7}$Sr$_{0.3}$MnO$_3$, both hard X-ray excitation at about 6 keV (Spring-8) and soft X-ray excitation at 833.2 eV that maximizes reflectivity near the La 3d$_{5/2}$ absorption edge (ALS) were used. The sample configuration and experimental geometry are shown in Fig. 14. In this work, Gray et al. measured rocking curves at both energies for core levels representing all elements in the sample, as well as valence levels in the room-temperature MEWDOS limit. The detailed analysis of these results appears elsewhere, but as some indication of the effects seen, Fig. 15 shows the final results of fitting X-ray optical calculations based on the specially written program due to Yang [43] to the experimental rocking curves for all elements. Note the presence of both the primary Bragg reflection rocking curve from the multilayer period $d_{ML}$, and the Kiesig fringes associated with reflection from the top and bottom of the multilayer that is derived is shown in Fig. 16. Notable here is that it was also found that the multilayer period varied continuously from top
Fe//MgO interface, from which it was also concluded that very little oxidation occurs at the interface [45]. For the Ta/FeCoB/MgO tunnel junction, it was possible to derive the detailed concentration profiles of B after annealing the sample to improve its tunnel magnetoresistance, including the B diffusion into the Ta and the MgO [46].

Element-resolved densities of states from single-crystal Bragg reflection: For completeness, I will briefly discuss work by other groups in which Bragg reflection from crystal planes is used to create a standing wave that can be scanned through a unit cell, thus modulating both core-level and valence-level intensities. Via the simple model that valence-level intensities in the MEWDOS limit represent element-projected densities of states multiplied by appropriate free-atom differential photoelectric cross sections, one can use core-level spectra to resolve valence spectra into their elemental components. Woicik et al. [38] have illustrated this for several solids (Cu, Ge, GaAs, InP, and NiO) and compared the results with theory.

More recently, Theiss et al. [39] have studied SrTiO$_3$ using this method, and some of their results are summarized in Fig. 20. The data shown here represent scanning the standing wave along the [1 1 1] direction by varying the photon energy through the Bragg condition (the second method shown in Fig. 13), with the planes of constant phase shown in Fig. 20(b). The variation of reflectivity and various core-level intensities with photon energy is shown in Fig. 20(d), and the modulation of the valence-band spectrum with photon energy in Fig. 20(c). The core-level variations have then been used in a set of linear equations to self-consistently...
resolve the valence-band spectrum into the element-specific components shown in Fig. 20(a). These results have been compared to density functional theory, with good agreement, although the effective cross sections needed to bring theory into agreement with experiment appear to differ from those expected on the basis of the free-atom, and may indicate that a more complex theoretical treatment is needed to analyze such element-resolved densities of states. Nonetheless, this is yet another very promising tool for studying electronic structure via hard X-ray standing-wave photoemission.

4.4. Standing-wave HXPS: future directions and limitations

SW-HXPS thus represents a powerful new addition to our experimental tools for studying the variation of composition, chemical state, and magnetic order in buried layers and interfaces. An important limitation is of course that the sample must be grown as, or on top of, a multilayer of sufficiently high quality to yield good reflectivity and resultant high standing-wave amplitude. For polycrystalline systems, this is rather easily achieved by growing samples on substrates available from current multilayer mirror...
As a final comment, the fully quantitative analysis of SW-HXPS involves varying some geometric parameters such as layer thicknesses and interface roughness or intermixing between layers over a number of choices so as to best fit the experimental data [42,44,46], and this must be done in a careful way so as to avoid false minima in some sort of best-fit criterion, and thus incorrect conclusions. However, the fact that the SW photoemission measurement inherently includes the phase between incident and reflected waves should make its data analysis simpler as compared to complementary studies of multilayer systems involving photon-in-photon-out X-ray scattering, either off- or on-resonant excitation energies [55], in which this phase information is not explicitly in the data but must somehow be retrieved by another trial and error fitting process. The direct consequence of having this phase information in SW-HXPS (or SW-SXPS) is that the movement of the standing wave is sensed in real space through the localized photoemission process, rather than only being observable in reciprocal space through the scattering process.

5. Concluding remarks

Making use of angular resolution and standing-wave excitation thus provides a number of exciting possibilities for the future of hard X-ray photoemission. With HARPES, the $\hat{k}$-resolved bulk electronic structure of materials can be studied, as illustrated for a dilute magnetic semiconductor. HXPD should be useful for studying bulk structure, including the site occupations of dopants. Standing-wave HXPS can probe buried layers and interfaces via multilayer reflectivity, as illustrated for several systems of relevance to spintronics and semiconductor technology, or the elemental makeup of valence electronic structure via Bragg reflection technology, as discussed above. For epitaxial systems, the sample synthesis is more difficult, but in fact, multilayers are often used in such studies in order to linearly amplify and identify the unique effects occurring at interfaces [47]. Another method my group has used is to create an epitaxial multilayer substrate from a binary system that is known to grow well (e.g. GaAs/AlAs or SrTiO$_3$/La$_{0.67}$Sr$_{0.33}$MnO$_3$), and then as a last step to grow the desired sample on top of this (e.g. Fe/MgO or SrTiO$_3$/BiFeO$_3$, respectively).

SW-HXPS is clearly complementary to the other most powerful tool for such buried interface studies, transmission electron microscopy with electron energy loss spectroscopy (TEM-ELS), which can yield truly atomic-resolution profiles through interfaces with element specificity [48] and even local structural information via diffraction analysis [49]. By comparison, SW-HXPS is non-destructive of the sample and can provide more direct information on chemical and magnetic states of different elements through chemical shifts, multiplet splittings and other fine structure in core spectra, as well as through variable-polarization dichroism measurements. Depth-dependent valence-band densities of states can also be studied more directly with SW-HXPS, in principle also with spin resolution in the future as much faster spin detection schemes for photoemission are developed [50,51]. The same complementary continuum of possibilities over photon energy noted for SARPES and HARPES above also exists for standing-wave studies, with both SW-HXPS and SW-SXPS being promising for the future. Finally, building on some prior SW-SXPS studies in photoelectron microscopy which have shown the ability to measure truly three-dimensional images with depth resolution [52,53], SW-HXPS should also be useful in hard X-ray photoelectron microscopy (HXPEEM), for which some first proof-of-principle measurements have already been obtained [54].

Fig. 20. Determination of element-specific contributions to the density of states in SrTiO$_3$ using crystal Bragg-reflection standing-wave photoemission. (a) The final decomposition of the valence spectrum into its elemental components. (b) The nature of the standing wave fronts parallel to (1 1 1) planes in the crystal. (c) The variation in the valence spectra as the photon energy is scanned through the Bragg condition. (d) The variation of core-level intensities with photon energy (bottom scale), together with the variation in reflectivity (top scale), both as a function of photon energy.

From Ref. [39].

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from crystal planes, as illustrated for a transition metal oxide. It is also clear that the intensities of current and planned beamlines and spectrometers permit studying dopants down to the 1% level if not lower, thus much expanding the range of interesting materials and physical properties that can be studied. Future measurements using variable polarization, spin detection, and photoelectron microscopes are also very promising.

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