

# Bulk-sensitive properties from high-energy spectroscopies

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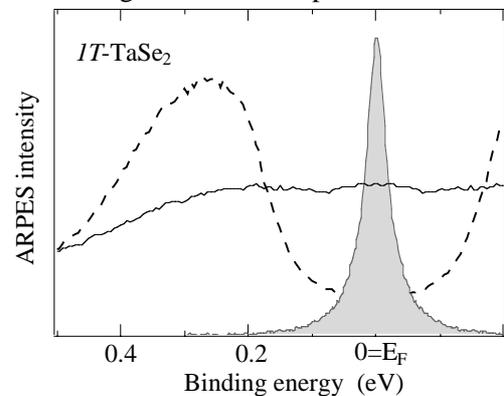
## Abstract

In this talk I review ongoing experimental efforts to develop truly bulk-sensitive spectroscopic probes of the electronic states in strongly correlated materials. The present reference is high-resolution angle-resolved photoelectron spectroscopy (ARPES), which provides a detailed view of the quasiparticle (QP) excitations, but suffers from a large surface sensitivity. The possibility of increasing the probing depth by extending high-resolution ARPES to the soft x-ray regime has already been demonstrated, and is actively pursued at various synchrotron radiation laboratories. Further steps in this direction are possible, either moving to all-photon spectroscopies, or using more energetic x-rays at high-flux, high-brilliance SR sources.

The discovery of high temperature superconductivity, and of other unconventional properties in the cuprates, has been a driving force in the development of ARPES with high energy and momentum resolution. Recent progress includes a better awareness of so-far unexploited features through more sophisticated data analysis, and a dramatic improvement in the performance of the photon sources - including SR sources - and electron analyzers. The whole field of strongly correlated systems has taken advantage of this development.

Modern ARPES is almost an ideal technique in this field because: i) it allows the properties of QPs with well-defined momentum to be studied, and ii) the QP spectrum exhibits both low-energy *coherent* features, and additional *incoherent* structure reflecting the dressing of the QP.

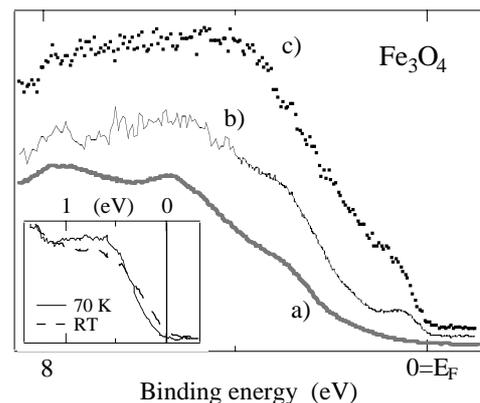
**Figure 1.** ARPES spectra ( $h\nu=21.2$  eV) of  $1T$ -TaSe<sub>2</sub>, measured at  $k=k_F$  above (dashed) and below (solid line) a surface M-I transition. A normal QP lineshape (shaded) measured on the Fermi liquid reference TiTe<sub>2</sub> in the same conditions, is shown by comparison. All spectra have been symmetrized around  $E_F$ .



This is illustrated by the example of Fig. 1. The transition (at  $\sim 260$  K) from a "bad metal" to a strongly correlated insulator in the quasi-2D system  $1T$ -TaSe<sub>2</sub> is reflected in characteristic spectral changes at the Fermi surface. The weak QP peak at  $E_F$ , disappears, while an energy gap opens, and a sharp satellite grows out of a broad incoherent sideband, in good agreement with the picture of the Mott transition from DMFT theory [1]. This example illustrates at the same time the power of ARPES, and its major shortcoming. Transport measurements in fact demonstrate that  $1T$ -TaSe<sub>2</sub> remains metallic at all temperatures, so that the *surface* M-I transition revealed by ARPES (but missed by transport!) is not a bulk electronic property.

The *universal* curve of electron mean-free-path suggests that the probing depth of photoemission can be increased if the electron kinetic energy is increased. This is indeed confirmed by recent angle-integrated work at SPring-8 [2,3], which shows, for heavy fermion compounds and transition metal oxides, the expected large spectral differences between data collected in the UV and soft x-ray ( $h\nu < 1$  keV) range. More recently, soft x-ray ARPES band mapping was demonstrated in Japan [4] and at the ESRF [5], in spite of challenging technical requirements, and of theoretical concerns about the inhibiting role of electron-phonon scattering. Band mapping and gap spectroscopy will also represent the core scientific program of one branch of the ADDRESS soft x-ray beamline. The main features of this beamline now under construction at the Swiss Light Source will be presented during the talk.

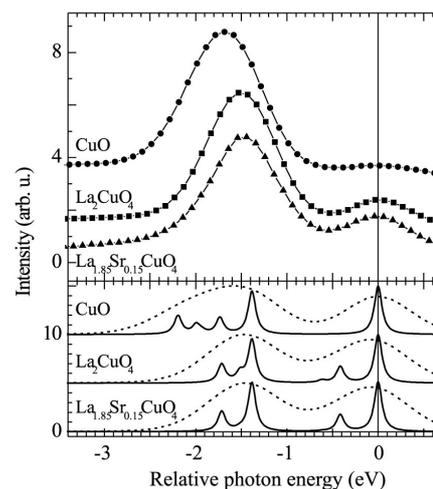
**Figure 2.** Comparison between : (a) PES (40.8 eV) and (b) XPS (1486 eV) spectra of a pristine Fe<sub>3</sub>O<sub>4</sub>(111) surface. The signature of the Verwey transition is visible in temperature-dependent XPS data (inset). Curve (c) is an XPS spectrum after a mild Ar<sup>+</sup> sputtering.



How bulk-sensitive really is soft x-ray ARPES? A quantitative answer to this question depends on the actual material and on electron kinetic energy, but it is instructive to consider by comparison the probing depth of valence PES with a traditional Al  $K_{\alpha}$  XPS ( $h\nu=1486$  eV, monochromatized) source. Figure 2 shows data from an as-grown shiny, mirror-like (111) surface of an  $Fe_3O_4$  single crystal. In the metallic phase, intensity at  $E_F$  is visible in the XPS spectrum (b), but completely absent in the surface sensitive UV spectrum (a). Moreover, temperature-dependent XPS spectra exhibit the expected changes associated with the opening of a gap at the M-I Verwey transition. Nonetheless, the surface contribution is not negligible, because intensity is recovered immediately below  $E_F$  when surface contamination is removed by a mild  $Ar^+$  sputtering (c).

Two different strategies can be envisaged to increase even further the bulk sensitivity of high-energy spectroscopies: i) to replace electrons by more penetrating photons as probes of electronic excitations, or ii) to "climb up" in the *universal MFP curve* towards the hard x-ray domain. In the first case, the radiative de-excitation following a core excitation is recorded, and energy-loss features in the emission spectrum reflect electronic excitations in the system. *Resonant* inelastic x-ray emission (RXES) is especially interesting. In this case the scattering cross section is largely and selectively enhanced, and absorption and emission are parts of a coherent second-order optical process, with specific (non-dipole) selection rules. RXES is also complementary to PES, because it probes *neutral* excitations. Figure 3 shows RXES spectra of three cuprate materials, measured at the Cu  $L_3$  ( $2p \rightarrow 3d$ ;  $h\nu \sim 930$  eV) edge. Each lineshape is dominated by a loss feature at  $\sim 1.5$  eV, which reflects CEF excited states of the Cu  $d^9$  ion. Their relative shifts are reproduced by a cluster calculation which yields

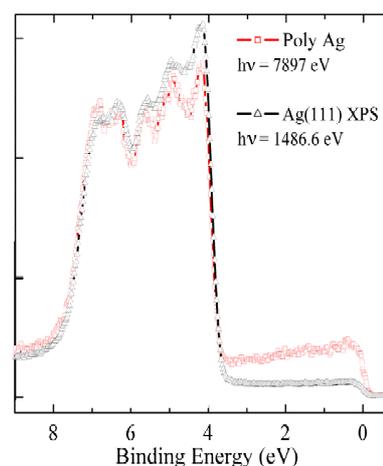
**Figure 3.** Cu  $L\alpha$  RXES spectra of selected Cu oxides. The elastic peak is at  $E=0$ , and the main loss structure is the envelope of Cu  $d$  CEF excitations.



the relevant CEF parameters [6]. The experimental resolution  $\Delta E \sim 0.8$  eV of the data, from the AXES spectrometer at beamline ID8 of the ESRF, is not yet sufficient to resolve the individual excited states. This will be possible with the Super-AXES spectrometer designed in collaboration with Politecnico di Milano for the RXES branch of the ADDRESS beamline, where a resolving power  $(E/\Delta E) \sim 10^4$  is foreseen.

Alternatively, higher energy x-rays from an intense undulator source can be used in a hard x-ray PES (HAXPES) experiment. Such an experiment faces the dramatic reduction ( $\sim E^{-3}$ ) of the PES cross section with excitation energy, and considerable technical challenges, especially if a resolution comparable to typical values of low-energy PES ( $\Delta E \sim 30-50$  meV) is to be achieved. This goal has been reached by the VOLPE spectrometer designed and built within a european collaboration, and now operational at the ESRF. Bulk sensitive data with a probing depth  $\sim 80$  Å and combined (electrons+photons) resolution  $\Delta E = 75$  meV at  $h\nu \sim 8$  keV have already been collected. An XPS/HAXPES comparison (Fig. 4) for silver illustrates the viability of the technique, and the expected enhancement of the relative "s" to "d" signal at the higher energy [7]. The contribution from the surface layer in this case is estimated to be less than  $\sim 5\%$ .

**Figure 4.** Valence band spectra of silver samples measured by conventional Al  $K_{\alpha}$  XPS, and by the VOLPE HAXPES spectrometer at beamline ID16 of the ESRF.



## References

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