Polarization dependent hard X-ray photoemission experiments for solids: Efficiency and limits for unraveling the orbital character of the valence band

J. Weinen [a,*], T.C. Koethe [b], C.F. Chang [a], S. Agrestini [a], D. Kasinathan [a], Y.F. Liao [c],
H. Fujiwara [b,1], C. Schüßler-Langeheine [b,2], F. Strigari [b], T. Haupricht [b], G. Panaccione [d],
F. Offi [e], G. Monaco [f,3], S. Huotari [f,4], K.-D. Tsuei [c], L.H. Tjeng [a,b]

[a] Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187 Dresden, Germany
[b] II. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, 50937 Köln, Germany
[c] National Synchrotron Radiation Research Center, 101 Hsin-Ann Road, Hsinchu Science-Park, Hsinchu 30077, Taiwan
[d] TASC Laboratory, IOM-CNR, Area Science Park, S.S.14, Km 163.5, I-34149 Trieste, Italy
[e] CNISM and Dipartimento di Scienze, Università Roma Tre, Via della Vasca Navale 84, I-00146 Rome, Italy
[f] European Synchrotron Radiation Facility, BP220, 38043 Grenoble, France

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ABSTRACT

We have investigated the efficiency and limits of polarization dependent hard X-ray photoelectron spectroscopy (HAXPES) in order to establish how well this method can be used to unravel quantitatively the contributions of the orbitals forming the valence band of solids. By rotating the energy analyzer rather than the polarization vector of the light using a phase retarder, we obtained the advantage that the full polarization of the light is available for the investigation. Using NiO, ZnO, and Cu_2O as examples for solid state materials, we established that the polarization dependence is much larger than in photoemission experiments utilizing ultra-violet or soft X-ray light. Yet we also have discovered that the polarization dependence is less than complete on the basis of atomic calculations, strongly suggesting that the trajectories of the outgoing electrons are affected by appreciable side-scattering processes even at these high kinetic energies. We have found in our experiment that these can be effectively described as a directional spread of $\pm 18°$ of the photoelectrons. This knowledge allows us to identify, for example, reliably the Ni $3d$ spectral weight of the NiO valence band and at the same time to demonstrate the importance of the Ni $4s$ for the chemical stability of the compound.

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1. Introduction

With bulk sensitivity being an important characteristic of HAXPES, another useful aspect of this technique appears to be the very pronounced dependence of the spectra on the polarization of the light. The selection rules in the photoexcitation process of electrons with linearly polarized light can in principle be used to identify the character of the orbitals contributing to the valence band [1–4]. Yet, transport of the photoelectrons to the surface and subsequent escape of the surface to the detector, involves scattering events that affect their angular intensity distributions. If the influence of these scattering processes can be estimated and the resulting effective polarization dependence can be made quantitative, one can obtain a very detailed understanding of the electronic structure of the material under study, especially when guided by theoretical
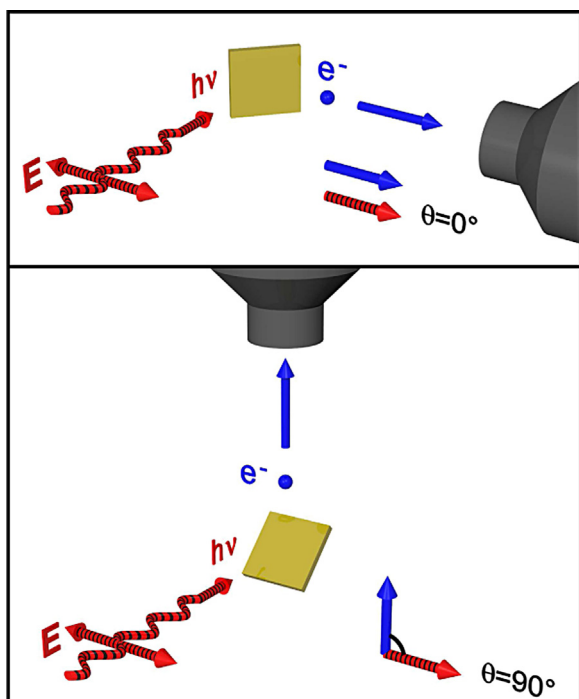
Fig. 1. Experimental geometry for different angles θ between the photon beam electrical field vector **E** (red, striped) and the momentum of the analyzed photoelectrons (blue). **E** is always horizontal, in the plane of the synchrotron storage ring. Top: analyzer mounted horizontally and parallel to the **E** vector, $\theta = 0°$. Bottom: analyzer mounted vertically and perpendicular to **E**, $\theta = 90°$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ab-initio calculations. The polarization dependent HAXPES experiments reported so far [1–4] made use of phase retarders to rotate the polarization of the light. The efficiency of the retarders to generate vertically polarized light, however, is about 0.8 only [1–4]. This hampers a reliable determination of the limits of polarization dependent HAXPES due to the inaccuracies in the characterization of the efficiency of the phase retarders.

Here we followed a different route: instead of rotating the polarization of the light, we altered the position of the electron energy analyzer, i.e. we used three different experimental geometries: in the first geometry the analyzer is placed in the direction of the linear polarization of the light, in the second perpendicular to the light polarization, and in the third at 45° [5]. This experimental set-up has the advantage that all the spectra can be taken with the full light polarization provided by the undulator beam line. We have carried out experiments on NiO, ZnO and Cu_2O as model systems for transition metal oxides. We measured the transition metal 2p and O 1s core levels, as well as the valence band of NiO.

2. Experimental

The experiments have been carried out at the Max-Planck-NSRRC HAXPES station at the Taiwan undulator beamline BL12XU at SPring-8, Japan, and at the VOLPE station placed at beamline ID16 of the ESRF in Grenoble, France [6]. The photon beam is linearly polarized with the electrical field vector in the plane of the storage ring (i.e. horizontal). Photon energies of about 6.5 keV and 7.7 keV have been used.

In the first geometry, the analyzer (MB Scientific A-1 HE) was mounted horizontally and parallel to the photon beam's electrical field vector. See top panel of Fig. 1. The maximum angular acceptance was limited to ±15.3° (30.5° total acceptance) by the circular opening of the first lens element. In the second
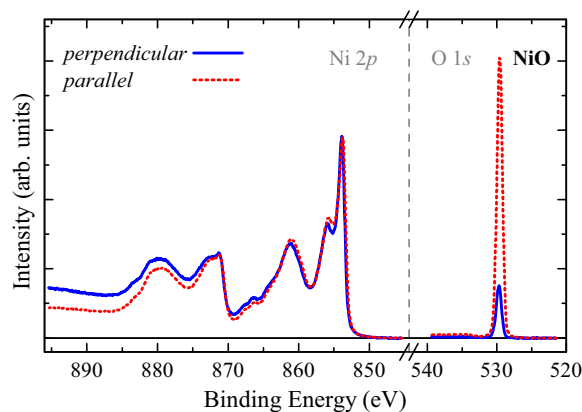
Fig. 2. HAXPES (photon energy 6.5 keV) spectra of NiO Ni 2p and O 1s core levels with $\theta = 90°$ (perpendicular) and $\theta = 0°$ (parallel).

geometry, the analyzer (MB Scientific A-1 HE) was mounted vertically, i.e. perpendicular to the electrical field vector and the Poynting vector of the beam. See bottom panel of Fig. 1. The maximum angular acceptance was limited to ±8.3° (16.6° total acceptance) by the circular opening of the first lens element. We have also utilized a third geometry, in which the analyzer (VOLPE/MB Scientific [6]) was put in the horizontal plane at 45° with respect to the electric field vector. A description of this is given in Ref. [5].

A NiO and a ZnO single crystal from SurfaceNet, Germany, were used. The Cu_2O sample was prepared by annealing a flat piece of oxidized copper metal in vacuum at 300° C [7]. All samples were measured at room temperature in a near normal emission geometry.

We have also performed X-ray photoemission (XPS) measurements for the NiO valence band using a Scienta SES-100 electron energy analyzer and a Vacuum Generators twin crystal monochromatized Al-K_α $h\nu = 1486.6$ eV source. The NiO single crystal was cleaved in-situ to obtain a clean surface.

3. Core levels

Fig. 2 displays the HAXPES Ni 2p and O 1s core level spectra of NiO taken with the photoelectron momentum parallel (red curves, $\theta = 0°$) and perpendicular (blue curves, $\theta = 90°$) to the polarization vector of the light. The photon energy was set at 6.5 keV and the overall energy resolution was 0.35–0.40 eV. The parallel vs. perpendicular spectra are normalized with respect to the Ni 2p main peak intensity. No corrections have been made to the spectra apart from a constant background subtraction. The line shape of the Ni 2p spectra is essentially identical to the ones published using also lower photon energies [8–13]. The O 1s spectrum shows a narrow single line demonstrating that the NiO sample is clean and of good quality. The relevant information that is contained in Fig. 2 is that the O 1s intensity is much lower for the perpendicular (blue curve) than for the parallel (red curve) polarization. This is qualitatively in agreement with the observations for s-orbitals in experiments in which the polarization has been varied using a phase retarder [1–4].

Making use of the fact that the degree of the photon polarization is identical for the two experimental geometries, we now can be quantitative concerning the physics underlying the change of the O 1s intensity with the photoelectron momentum. The expression for the angular dependence for the differential photoionization cross section is given by [14,15]

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 + \beta P_2(\cos\theta) + (\gamma \cos^2\theta + \delta)\sin\theta\cos\varphi \right] \qquad (1)$$