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Hard X-ray PhotoElectron Spectroscopy of transition metal oxides: Bulk compounds and device-ready metal-oxide interfaces

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ABSTRACT

Photoelectron spectroscopy is one of the most powerful tool to unravel the electronic structure of strongly correlated materials also thanks to the extremely large dynamic range in energy, coupled to high energy resolution that this form of spectroscopy covers. The kinetic energy range typically used for photoelectron experiments corresponds often to a strong surface sensitivity, and this turns out to be a disadvantage for the study of transition metal oxides, systems where structural and electronic reconstruction, different oxidation state, and electronic correlation may significantly vary at the surface. We report here selected Hard X-ray PhotoElectron Spectroscopy (HAXPES) results from transition metal oxides, and from buried interfaces, where we highlight some of the important features that such bulk sensitive technique brings in the analysis of electronic properties of the solids.

1. Introduction

Transition Metal Oxides (TMOs) are a vast class of materials with probably the most fascinating effects in solid-state physics [1]. The electron interaction and the competing forces the electrons experience in TMOs produce, on a very small energy scale, the intricate balance between band formation and electron-correlation effects, i.e., itinerancy vs. localization. In TMOs, only a full identification of the relevant charge, orbital and spin degrees of freedom of the metal ions involved may provide both a more complete picture of their complex properties and the basis for novel applications, termed in recent years as spintronics and orbitronics [2,3].

High-energy electron spectroscopies, like X-ray Absorption Spectroscopy (XAS) and PhotoElectron Spectroscopy (PES), have been extensively used to study the exotic electronic and magnetic properties of TMOs, like giant magneto-resistance, superconductivity and metal-insulator transitions. PES is a powerful tool to investigate the electronic properties of materials, with impressive technical achievements in terms of momentum and angular resolution, and, in case the high intensity and large tunability of synchrotron radiation is used, PES is able to cover a large dynamic range in energy, by studying excitation spectra from several thousands of eV down to a few eV and close to the chemical potential, where one can measure directly the behavior of the 'dressed' electrons, e.g., the quasi particles.

Over the last five decades, PES experiments with synchrotron radiation mostly exploited one of the key features of the technique, i.e., its surface sensitivity. By tuning the kinetic energy of photoelectrons to the minimum of their (inelastic) mean free path in the solid, the measurement is sensitive to the topmost atomic layers only. In the case of TMOs, such extreme surface sensitivity may turn into an obstacle: in fact, many TMOs adopt a surface electronic configuration different from that of the bulk, as due not only to the 'classic' structural surface reconstructions, but also because the Coulomb interaction and in general the electronic correlations are severely modified by the broken symmetry that the surface represents. It is important to underline that the problem of not being able to measure the bulk electronic structure cannot be solved even by having the sample as a single crystal with a perfect surface termination. The surface will always have a different electronic structure than the bulk, and this is especially true for strongly correlated oxides since small variations of the surrounding of the atomic-like *d* or *f* orbitals will already have a big impact on the band structure. Most TM oxides are insulators due to strong electron correlation effects arising from the localized character of the TM ions; often, the role of the oxygen *2p* band and its energy balance with respect to the *s* and *d* states defines the metallic-insulating character of the material, as beautifully described by the Zaanen-Sawatzky-Allen phase diagram in terms of charge transfer energy between oxygen-*2p*-to-*3d* transition-metal [4]. Standard PES in these materials is severely

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handicapped by the fact that the high oxidation state is not stable at the surface, i.e., CrO_2 for example is reduced to the more stable Cr_2O_3 at the surface [5,6].

The increase of the information depth achievable in PES has always been a major target, tackled in recent years with the development of Hard X-ray PhotoElectron Spectroscopy (HAXPES), where one exploits the augmented mean free path of high kinetic energy electrons [7,8]. HAXPES experiments were originally pioneered by Pianetta and Lindau in 1974, and have recently been revived by several research groups since 2003 [9–14]. The use of synchrotron radiation made possible to circumvent the strong decrease of photoionization cross section, reaching good statistics and medium energy resolution (down to 50 meV) at kinetic energies as high as in the 10 keV range, corresponding to an information depth of several nm, and a contribution of the surface reduced down to a few percent. HAXPES experiments devoted to the understanding of TMOs properties have been the leading activity at the ‘infancy’ stage of HAXPES; such approach has been recently extended to the analysis of TMO-based buried interfaces and to the ‘in-operando’ spectroscopy, where device-ready heterogeneous interfaces are studied in working conditions with no need of surface preparation. Aim of this paper is to give selected examples of the HAXPES research on TMOs, focusing on the capabilities of the technique in both fundamental and applied physics.

2. Spectral enhancement of *s* states

A peculiar characteristic of HAXPES experiments is the strong decrease of photoionization cross section at high kinetic energies with respect to the VUV and soft X-ray range. Theoretical and experimental papers clearly demonstrate that an overall decrease up to a factor 10^{-6} can be found when passing from soft to hard X-ray regime (i.e., for a few hundred eV of kinetic energy to several thousands) [15–17]. Despite that, measuring valence band HAXPES allows for the determination of the Fermi level and/or of the surface carrier accumulation of complex oxides, intrinsic or under doping, with truly bulk sensitivity and no contribution from surface charge accumulation. Interestingly, it has been soon clear that a further parameter enters into play, namely the relative ratio of states with different symmetry that strongly favors extended *s* states with respect to localized *p*, *d* and *f* ones [18,19]. Such differences and the experimental observation of a similar enhancement of *s* states for many metal oxides turned to be a new and unique probe of metal *s* character within the total density of states of an oxide [20–23]. Important examples of such approach include doped ZnO, CdO, In_2O_3 and SnO_2, systems with potentially relevant applications in optoelectronic and spintronics, where doping produces a degenerate electron gas with carrier concentrations in the range up to about 10^{21} cm^{-3}. This leads to occupation of a conduction band derived mainly from metal *4s* or *5s* states, hence HAXPES experiments possess the right sensitivity to detect metallic vs. insulating character near the chemical potential.

An example of the spectral changes occurring for the different orbital contributions to the spectrum of the valence states measured with soft and hard x-ray excitation energies is shown in Fig. 1 for a NiO film of 15 nm of thickness grown on Ag(0 0 1) [24]. The red curve represents the NiO valence band (VB) recorded with the standard laboratory source Mg *Kα* and displays the well-known lineshape in which the visible peaks are ascribed to the multiplet structure of the Ni *3d* levels [25]. On the opposite, the NiO VB recorded for photon energy of 8 keV presents a lineshape that is markedly different from the one measured with a standard excitation energy. This is essentially due to the change in the relative cross section values between levels with different symmetries when passing from low to high kinetic energy regimes. As it has been shown in several studies [26,27], the weight of the *s* and *p* levels in the HAXPES spectra are enhanced with respect to the *d* contribution. A clear illustration of this process is given in these spectra by the rise (in the high energy regime) of the *2s* peak of oxygen which is located at about 22 eV of binding energy. Similarly to that, the two structures having a significant growth of intensity at high kinetic energy, located at 6 and 8 eV of binding energy, can be respectively assigned to the *p* level of O and partly to the *s* level of Ni, while the sharp peak close to the Fermi energy has predominantly *d* character.

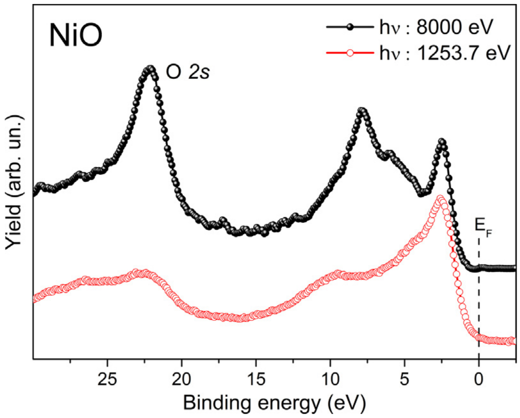

Fig. 1. Photoelectron spectra of the valence band region of NiO (from a 15 nm NiO film deposited onto Ag(0 0 1) surface) recorded with 8 keV of photon energy (black spheres) and 1253.7 eV of photon energy (open red spheres).

PES studies of the *3d* transition metal elements usually concern the *2p* and *3s* core levels. Being the binding energies of such orbitals in between 400 eV and 1000 eV, photoelectron emission from these levels can be promoted employing soft X-ray quasi-monochromatic radiation provided by laboratory or synchrotron radiation sources. Few attempts to probe the *1s* levels and the Auger transitions associated with the formation of a *1s* core hole of TMOs were performed using a hard X-ray source equipped with Cu, Ti or Cr anodes [28–36]. HAXPES *1s* spectra obtained at synchrotron radiation sources have been recently reported, as for Ni *1s* for the metal and nickel monoxide [37,38], Mn *1s* for MnAs and $Bi_{1.91}Mn_{0.09}Te$ [39], and Fe *1s* for Fe_2O_3 [40]. In absence of spin-orbit coupling and exchange splitting effects, the spectrum for the photoelectron emission from the *1s* levels of the TMOs has a relatively simple spectral shape, eventually with the presence of satellites occurring at some eV from the main peak. Noticeably, a recent study of the Ti *1s* core level spectrum of $SrTiO_3$ has shown the presence of a satellite located at a distance of 5 eV on the high binding energy side of the Ti *1s* peak, in addition to the well-studied structure at 13 eV that is typically observed for the Ti *2p* core line. [41] This work demonstrates that the presence of the satellites in the Ti *1s* spectrum originates from the crystal-field splitting of the metal *3d* orbitals and ligand *2p*–metal *3d* charge transfer among Ti and the surrounding oxygen ions.

The decrease of the photoionization cross section for the deep *1s* core levels in the hard x-ray energy range is usually slower than those with larger orbital quantum number, making them an interesting way to probe systems with small concentrations of *3d* TM ions, especially when the *2p* spectra are negligible or overlapped to other spectral features. This case is shown in Fig. 2 where, in absence of other detectable spectral lines, the Fe *1s* core level spectrum has been measured for iron-doped bismuth selenide (Fe:Bi_2Se_3) and compared to the spectra of bulk iron oxide (FeO_x) and Fe metal. In the figure, all the spectra are aligned on the binding energy scale to the maximum peak intensity. While in the case of metallic Fe a single peak was reasonably expected, the spectrum of