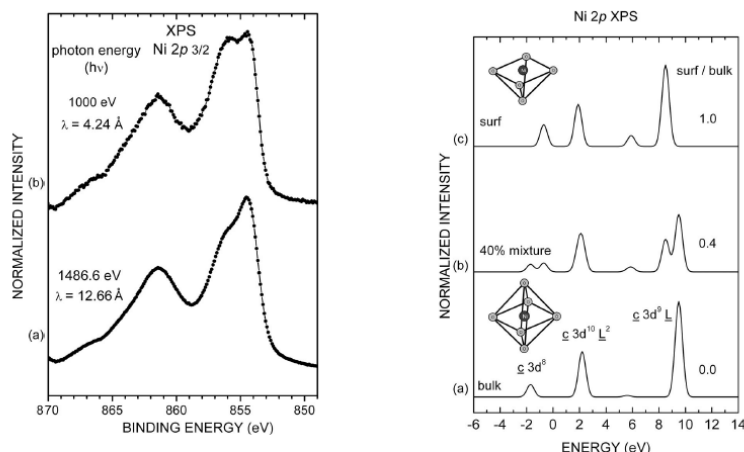UNIVERSIDAD DE MÁLAGA

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CONFERENCIA

The Electronic Structure of NiO by means of Electron Spectroscopies and theoretical calculations

Keywords: Photoemission, X-ray absorption, NiO/oxide interface, Local density approach calculations

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Surface effects in the Ni 2p x-ray photoemission spectra of NiO

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We report experimental and theoretical evidence of surface effects in the Ni 2p x-ray photoemission spectra (XPS) of NiO. The Ni $2p_{3/2}$ surface-enhanced XPS of a NiO sample show a relative enhancement of the intensity of the known satellite at 1.5 eV higher binding energy from the main line, indicating a considerable surface contribution of this satellite. The results are discussed in terms of bulk-octahedral and surface-pyramidal Ni symmetries. Other contributions, like nonlocal screening effects, cannot be neglected.

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I. INTRODUCTION

Nickel oxide is one of the most investigated transition metal oxides, whose electronic structure has been controversial for years. Not only has the nature of the band gap been a matter of discussion, but also the electronic structure of their surfaces, defects, etc. Nowadays, it is accepted that NiO is a $3d^8$ charge transfer oxide and the ground state is a mixture of $3d^8$, $3d^9\underline{L}$, and $3d^{10}\underline{L}^2$ configurations.[1–3] This gives rise to a complex line shape of the experimental spectra when using spectroscopic techniques, in particular x-ray photoemission spectroscopy (XPS). The Ni 2p photoemission peak line shape of NiO shows a multipeaked structure which has been widely discussed in the literature. Nowadays, it has been shown that cluster calculations of the Ni 2p photoemission spectrum for a NiO$_6$ cluster give rise to three different peaks, according to the above description of the electronic structure. However, the very-well-known additional shoulder separated by 1.5 eV at higher binding energies from the main line is absent in those calculations.[4] This satellite appears only when the calculations are extended to a larger Ni$_7$O$_{36}$ cluster. As a consequence of that, the satellite was called a *nonlocal screening satellite* and was explained as a screening process due to oxygen atoms belonging to the outer NiO$_6$ clusters.[4] In this work we present additional experimental evidence and a theoretical model that show that the origin of the satellite is not only due to nonlocal effects, but also to surface effects, being its main contribution that surface effects are separated from the nonlocal screening model. These experimental results are theoretically interpreted by cluster model calculations in terms of the reduced symmetry at the surface (see Table I). The reason for using single NiO$_5$ and NiO$_6$ clusters in our calculation is to highlight the surface contribution of the 1.5-eV satellite, even without including the nonlocal screening effect from adjacent clusters. In this picture, the main line ($\underline{c}3d^9\underline{L}$) of the XPS spectra of surface Ni ions shifts 1.0 eV towards higher binding energies, thus significantly contributing to the satellite intensity. These conclusions are completely consistent with recent results showing a splitting of the Ni e_g states at the NiO surface[5] and suggest a new interpretation of the Ni 2p XPS spectra, especially those concerning nanostructured NiO, where surface effects are dominant due to the large surface-to-volume ratio.

The so-called nonlocal satellite in the Ni 2p XPS spectra has been conventionally assigned to the presence of Ni^{3+} species at the NiO surface.[6] In general, it has been observed that the intensity of this satellite increases with the creation of defects. For instance, Uhlenbrock *et al.*[7] concluded that Ar bombardment of a freshly cleaved NiO (100) surface produces the formation of Ni^{3+} species and the simultaneous reduction to Ni^0 when analyzing the intensity of the satellite with respect to the main line. However, it is well known that Ar bombardment produces oxygen vacancies due to preferential sputtering of oxygen, leading to the reduction of Ni atoms to metallic Ni.[8] Other interesting systems to study the effect of defects in NiO are highly defective 3–5-nm NiO nanoparticles, whose Ni 2p XPS spectra show a clear enhancement of the relative intensity of the satellite with respect to the spectrum of a NiO single crystal.[9] This effect was related to the good catalytic properties of the nanoparticles and explained as due to the presence of Ni^{3+} defects.

TABLE I. Parameters of the cluster model calculation. Δ, charge transfer; U, electron repulsion; $pd\sigma$, p-d hybridization; Q, B, C, Racah parameters; $10Dq$, crystal field.

Cluster parameters	
U	7.5
Δ	4.0
$pd\sigma$	1.5
Q	9.0
Multiplet parameters	
B	0.13
C	0.58
$10Dq$	0.1

However, in a posterior x-ray absorption spectroscopy (XAS) study of these nanoparticles,[10] Ni atoms were unambiguously characterized as high-spin Ni^{2+} species. This conclusion together with the results obtained in previous studies of hole-doped $Li_xNi_{1-x}O$ (Refs. [11] and [12]) make doubtful the existence of Ni^{3+} defects at the NiO surface. Other authors found a dependence of the intensity of the satellite on the emission angle of a NiO single crystal.[13,14] They concluded that the satellite could be associated with the surface Ni atoms but no appropriate theoretical model was proposed to explain the experiment. Other interpretations appearing in the literature assign the satellite to $\underline{c}3d^{10}\underline{L}^2$ (Ref. [15]) states or $\underline{c}3d^9$ multiplets.[16] Therefore, the origin of the satellite at 1.5 eV higher binding energies with respect to the main line in the Ni $2p$ XPS spectra in NiO remains unclear.

As mentioned above, the interpretation of the satellite as a nonlocal process is the most accepted theory at present. This model is supported by experimental results in the systems: $Ni_xMg_{1-x}O$ (Ref. [17]) and one epitaxial NiO monolayer grown on MgO single crystal.[18] In these systems, the nonlocal satellite is absent as corresponds to systems where, in spite of Ni atoms are octahedrally surrounded by oxygen atoms, no second neighboring oxygen atoms exist. The nonlocal screening model suggests that the satellite structure is intrinsic for bulk NiO. However, when the calculations are restricted to a Ni_6O_{30} cluster, unexpectedly the intensity of the satellite increases. The authors conclude that this could be due to a different coordination of the cluster with the core hole—i.e., fivefold to sixfold.[4] In turn, the model does not explain the absence of the satellite in the Ni $2p$ XPS spectrum of La_2NiO_4 as corresponds to a purely octahedral Ni compound.[14] Other recent results for nanoscopic NiO systems, where the large surface-to-volume ratio permits the detection of surface effects, concern NiO nanoparticles and planar NiO nanoislands grown on highly oriented pyrolitic graphite (HOPG).[5] In these systems, the O $1s$ XAS spectra show a splitting of the Ni e_g states at the surface of the nanostructures. This splitting has been explained as arising from the pyramidally coordinated Ni atoms at the surface. Similar surface states have also been experimentally observed[19,20] and calculated for a NiO (100) surface using local density approach (LDA) calculations including electron repulsion.[21] The effect of the large surface-to-volume ratio on the Ni $2p$ XPS spectra has been studied in NiO nanoparticles, giving an increase of the satellite intensity.[22]

It seems reasonable to think that the above splitting of the Ni $3d$ levels at the surface could also be reflected in the Ni $2p$ XPS spectra. To investigate this possibility, we have performed two simple experimental XPS measurements of a bulk NiO sample. In XPS there are two main techniques to make the spectrum more sensitive to the surface by minimizing the inelastic mean free path[23] (λ): using a grazing takeoff angle and reducing the kinetic energy of the photoelectrons to approach the minimum of the universal curve. We present below the Ni $2p$ XPS spectra of a NiO sample measured at different takeoff emission angles and at different photon energies.

II. EXPERIMENTAL DETAILS

A NiO thin film (200 Å) was grown *in situ* by reactive evaporation of Ni following conventional methods on
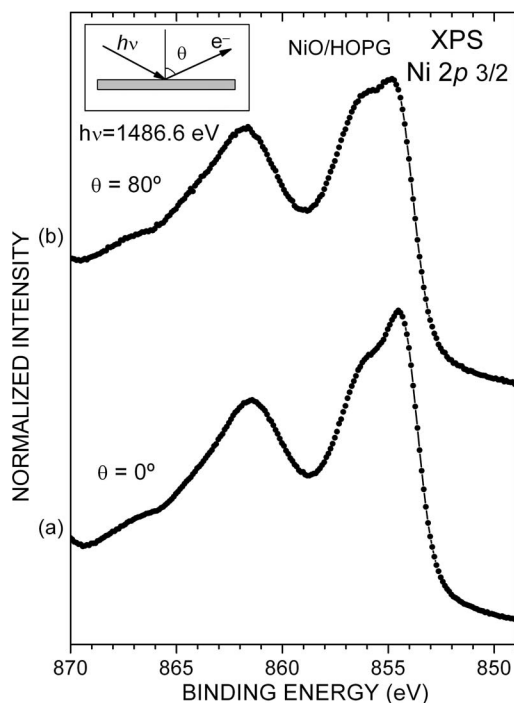

FIG. 1. Experimental XPS spectra of a NiO thin film measured with Al anode at (a) 0° and (b) 85° emission angle (θ). The inset shows the geometry of the measurements.

HOPG.[5] The measurements at different takeoff angles were performed with a CLAM4 electron analyzer in our laboratory whereas the measurements at different photon energies were performed at the PM4 beamline of the Synchrotron BESSY (Berlin) using a Phoibos analyzer. The energy resolution was approximately 0.8 eV in both cases and the angular resolution was about ±3°.

III. RESULTS

The Ni $2p_{3/2}$ XPS spectra of the NiO thin film taken with Al $K\alpha$ radiation at various emission angles (θ) are shown in Fig. 1. The spectrum taken at $\theta=0°$ [Fig. 1(a)] agrees with that of a NiO single crystal.[4] The spectrum taken at $\theta=80°$ [Fig. 1(b)] shows a clear enhancement of the intensity of the satellite at 856.0 eV with respect to that measured at $\theta=0°$. Band dispersion and matrix element effects are important for valence levels at low energies, like angle-resolved photoemission spectroscopy (ARPES), but are not expected to significantly influence the core-level spectra at higher energies (XPS). Therefore, the results seem to indicate that the satellite contains a considerable surface contribution. Thus, the first experiment is qualitatively consistent with the interpretation made in this paper.

In Fig. 2, the Ni $2p_{3/2}$ XPS spectra of the NiO thin film taken at different photon energies are depicted. The kinetic energy of the photoelectrons in the conventional spectrum taken with Al $K\alpha$ radiation [Fig. 2(a)] is about 630 eV, whereas in the spectrum taken in the synchrotron at 1000 eV photon energy [Fig. 2(b)] is about 145 eV, thus giving values
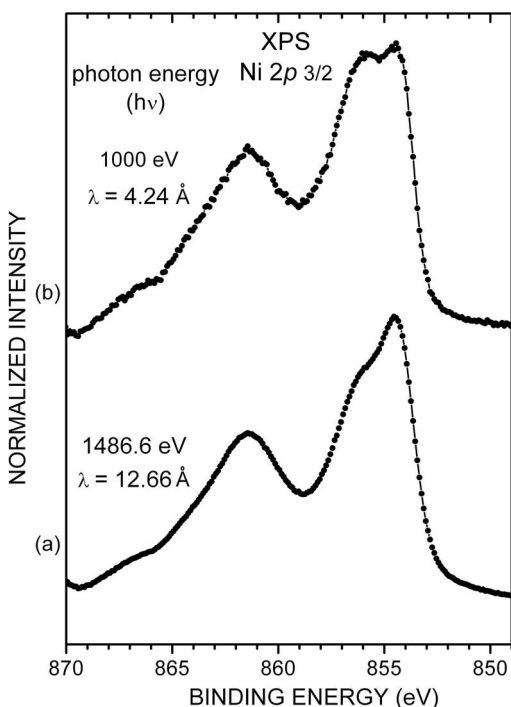
FIG. 2. Experimental XPS spectra of a NiO thin film measured at (a) 1486.8 eV and (b) 1000 eV photon energies. The measurements were performed at normal emission angle ($\theta = 0$).

for the inelastic mean free path of 12.66 Å and 4.24 Å, respectively.[20] The spectrum taken with synchrotron light at 1000 eV shows a large increase of the relative satellite intensity. The changes of the cross section with energy affect all the component of the core-level spectra and cannot account for the change of only one component as observed in the experimental data. Therefore, these results are again consistent with the interpretation that the satellite at 856.0 eV has a large surface contribution. However, detailed XPS quantitative analysis of both peaks indicates that the intensity of the satellite is too high to be explained as only due to the surface contribution. This seems to indicate that other processes, like nonlocal screening, could also contribute to the satellite intensity.

In order to give an interpretation to the experimental data, we have performed cluster model calculations to theoretically reproduce the Ni $2p$ core-level spectra. The clusters were NiO_6 in octahedral symmetry (bulk) and NiO_5 in pyramidal symmetry (surface). The ground state was expanded in the $3d^8$, $3d^9\underline{L}$, and $3d^{10}\underline{L}^2$ configurations, where $\underline{L}$ denotes a symmetry adapted O $2p$ hole.[24] The final state was expanded in the $\underline{c}3d^8$, $\underline{c}3d^9\underline{L}$, and $\underline{c}3d^{10}\underline{L}^2$ configurations, where $\underline{c}$ here denotes a hole in Ni $2p$ core level. The Ni $2p$ photoelectron spectra were then calculated using the sudden approximation.[18]

The parameters of the model were the charge transfer energy $\Delta = 4.0$ eV, the Mott-Hubbard repulsion $U = 7.5$ eV, the core-hole potential $Q = 9.0$ eV, and the p-d transfer integral $T_\sigma = 2.6$ eV.[25] These values give the best agreement with the experiment and are in agreement with previous estimates. The multiplet splitting was given in terms of the Raccah parameters $B = 0.13$ eV and $C = 0.58$ eV, as well as the crys-
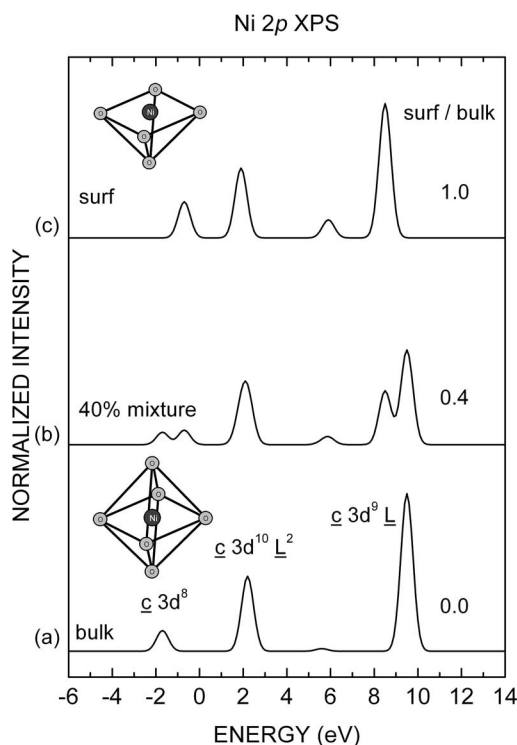

FIG. 3. Results of the cluster calculations performed in (a) octahedral symmetry, (b) a combination of a 60% octahedral and 40% pyramidal symmetries, and (c) pyramidal symmetry.

tal field parameter $10Dq = 0.10$ eV. The transfer of the x^2-y^2 level involved T_σ in both octahedral and pyramidal symmetries. The transfer of the z^2 level involved also T_σ in octahedral symmetry, but only $\frac{2}{3}T_\sigma$ in pyramidal symmetry due to the lack of the apical O.[26]

Figure 3 shows the results of the calculation in octahedral (a) and pyramidal (c) symmetries. For the bulk NiO_6 cluster, the calculation presents the standard $\underline{c}3d^9\underline{L}$, $\underline{c}3d^{10}\underline{L}^2$, and $\underline{c}3d^8$ peaks. For the surface NiO_5 cluster, the calculations show these peaks but the energy spread is smaller (the additional peak in the spectrum is due to the different hybridization of the x^2-y^2 and z^2 levels). The overall energy separation between the peaks is roughly given by $\Delta E^2 = (Q - \Delta)^2 + 4T_{eff}^2$. The smaller energy spread above is attributed to the reduced T_{eff} in pyramidal symmetry.

The $\underline{c}3d^9\underline{L}$ peak at the surface is shifted 1.0 eV toward lower energies with respect to the bulk. These results suggest that the main line of the Ni $2p$ XPS spectra would come from the bulk, whereas the nonlocal structure would contain a considerable surface contribution. In fact, the mixture of 60% bulk and 40% surface (although nonlocal effects are also expected to contribute to the satellite intensity) components in Fig. 3(b) resembles the experimental Ni $2p$ XPS.

Other effects would also place a significant surface contribution at the nonlocal structure. For instance, the changes in the Madelung potential would affect the charge-transfer energy Δ and would also reduce the binding energy of the surface contribution by about 0.5 eV.[24] The differences in the hybridization were the key to interpret the O $1s$ XAS spectra of NiO nanostructures.[5] It is difficult to tell which of these effects dominates in the case of the Ni $2p$ XPS spec-

trum. A more realistic calculation considering all these effects would be needed to solve this question.

IV. CONCLUSIONS

In summary, we have studied the line shape of the Ni 2p photoemission spectra by means of experimental XPS spectra and theoretical cluster calculations. Surface enhanced XPS spectra show that the satellite has an important contribution from the surface Ni atoms. Cluster calculations performed in octahedral and pyramidal symmetry show that for surface Ni atoms (pyramidal) the main line of the spectrum is shifted by 1.0 eV towards higher binding energies, thus significantly contributing to the intensity of the satellite at 856.0 eV. However, the intensity of the satellite is much higher than that corresponding to a surface layer. This indicates that other effects like nonlocal screening have also to be taken into account. This interpretation of the Ni 2p XPS line shape opens a revision of the Ni 2p XPS spectra of NiO with a large surface-to-volume ratio.

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