

Electronic structure of epitaxial thin NiO(100) films grown on Ag(100): Towards a firm experimental basis

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Valence- and conduction-band states of NiO(100) thin films grown onto Ag(100) have been probed by photoemission (PE) and inverse photoemission (IPE) spectroscopy, respectively. In particular, emphasis is given to the empty states, for which contrasting data are reported on samples obtained by different procedures. The good quality of the investigated NiO sample surface has allowed us to deduce a reliable picture of the empty state spectral function. Exploiting \mathbf{k} resolution it was possible to disentangle the various orbital contributions and clearly fix their energy position, including that of the so-called ligand hole excitation. A combined PE and IPE analysis points towards the nearly intrinsic nature of the investigated NiO.

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INTRODUCTION

In the field of electron correlations in solids NiO definitely plays a key role. This material was considered long ago as a prototype system¹ to define the problems that arise in band concept if large electron-electron correlations are present.² Since then, a large amount of work on the electronic^{3,4} and magnetic⁴⁻⁶ properties of NiO has been done, but the long-standing problem of the full description and understanding of its electron states is, to some extent, still open.⁷⁻⁹

From the experimental point of view, photoemission (PE) and inverse PE (IPE) spectroscopies have given an important contribution to the comprehension of these problems as far as filled and empty states are concerned, respectively. For example, thanks to these techniques, it has been clarified¹⁰ that in NiO the gap is not associated to a Ni $d \rightarrow$ Ni d transition or, in other words, that NiO is not a Mott-Hubbard insulator. Rather, it was understood that the large band gap is indirectly caused by a large $d-d$ Coulomb interaction in combination with one-electron energies involving O $2p$ as well as Ni $3d$ states; this gives rise to a so-called charge-transfer insulator.

While for PE results on NiO a large set of data is available in literature,^{3,11-13} with a general consensus on the line shapes, concerning IPE some pioneering works have been carried out^{10,14-18} in the early 1980s, which shone some light on the problem of the electron addition excitations. Unfortunately, since those results were often influenced by some experimental difficulties, the situation for IPE is much less clear than for PE. In particular for *in situ* surface oxidation of Ni polycrystals^{14,19} and monocrystals,^{15,16} and for Ni heating in air,^{17,18} the grown “NiO” films have not been fully characterized in their structure and stoichiometry. Also bulk NiO monocrystals cleaved in vacuum have been measured by x-ray IPE:¹⁰ in this case severe charging effects took place. Following an unusual procedure, these were corrected by measuring the IPE positions at 200 °C for various sample currents and then extrapolating the spectrum corresponding to zero current. However, it has to be noted that, a few years later, the same groups did not succeed in getting any x-ray

IPE out of pure NiO and that strong (Li) doping was needed to avoid charging.²⁰ On the one hand it is therefore not surprising that the IPE results reported in all these works do not compare well with each other. On the other hand it is indeed surprising that these discrepancies have largely been overlooked and that a considerable amount of theoretical work and detailed speculations have been based on these empty states results.

Very recently the possibility of growing very well characterized NiO monocrystalline thin films has shown up both onto insulating (i.e., MgO, Ref. 21) and conducting²² substrates. In particular, for the latter case, this is obtained by evaporation of Ni in an O₂ atmosphere onto a nonreactive metal substrate, whose lattice parameter agrees with that of NiO. Thus it is now timely to give a firmer experimental basis to the subject of these NiO empty states. Besides the very high quality of the grown NiO, the thin-film structure prevents any problem of charging, even for IPE spectroscopy. We have therefore measured IPE spectra of NiO(100) thin films grown by such a method onto Ag(100). By studying the dispersion behavior of the various IPE features we are able to classify them as d - or sp -derived states and a d -like ligand hole structure at high energy is clearly shown. By combining these results to x-ray photoemission spectroscopy (XPS) taken on the same surfaces we find that the magnitude of the gap is similar to that previously found. A different aspect is instead related to the position of the Fermi level (E_F) which is near the middle of the gap. This is at variance with previous results^{3,10,17} which showed a strong pinning of E_F at the top of the valence band and were interpreted in detail³ as an intrinsic effect of “pure” NiO.

EXPERIMENT

The experiments herein reported refer to x-ray [$h\nu = 1253.6$ eV, with full width at half maximum (FWHM) = 0.8 eV] PE and UV ($h\nu = 9.4$ eV, FWHM = 0.7 eV) IPE, performed in an ultrahigh vacuum system (base pressure $< 7 \times 10^{-11}$ mbar) equipped with standard surface characterization techniques.²³ A clean Ag(100) surface has been obtained by repeated sputtering and annealing (up to 620 °C) cycles from a bulk single crystal and analyzed by low-energy

electron diffraction (LEED) and core-level XPS. NiO(100) has been grown by evaporation of pure Ni, at a rate of about 0.7 Ni monolayer (ML) per minute, in an O_2 pressure of 8×10^{-7} mbar. Different NiO film thicknesses have been prepared, in the 20–40-NiO-ML range obtaining very similar results in all cases. Film thicknesses were evaluated by a quartz microbalance. An alternative estimation based on the XPS Ni $2p$ and O $1s$ core-level intensities was furthermore performed using the escape depth values for inorganic compounds,²⁴ giving very similar results. Subsequent LEED and XPS analysis checks confirmed the correct structure and stoichiometry for NiO(100).

k -resolved IPE measurements have been performed with a 2–10- μ A sample current. Various incidence angles were set along the [011] direction, from normal incidence up to 20° off normal. All measurements have been collected at room temperature and no current dependent charging effects were detected whatsoever. Fermi level reference was obtained by the substrate Ag data both for PE and IPE.

RESULTS AND DISCUSSION

Due to the strong misfit (about 19%) between pure Ni and NiO lattice parameters it is known that thin NiO films do not grow properly onto Ni substrates.²⁵ In order to present the state of art concerning NiO empty states we will therefore compare IPE results for a NiO crystal cleaved *in situ*¹⁰ with those for a NiO sample obtained as a thick film by heating poly-Ni in air.¹⁷ Both these IPE studies have been combined with PE data and are, to date, the most commonly used references for a NiO standard to the authors' knowledge, at least concerning the region of the spectral function above E_F .

In a purely ionic picture NiO has a Ni $3d^8$ O $2p^6$ outermost electronic configuration in the ground state. Due to the strong localization of the Ni $3d$ orbitals, an electron addition excitation involving a $3d$ electron, like those taking place in IPE, leaves the system with a localized extra particle: since configuration interaction processes occur, two different final states are possible, namely d^9 and $d^{10}L$. In the latter a ligand-to-metal charge transfer takes place to further increase the d population (here L indicates the presence of a ligand hole). Their energies give relevant information for determining the on-site Coulomb interaction (U), and the charge-transfer energy (Δ).²⁰ Following the notation used above and neglecting the hybridization shift of the ground state due to Ni $3d$ -O $2p$ mixing, U can be defined as the energy needed for a $d^8 d^8 \rightarrow d^7 d^9$ transition, i.e., a d - d hopping event, while Δ is the cost of a $d^8 \rightarrow d^9 L$ excitation, which represents the electron transfer from an O $2p$ band into the transition-metal $3d$ orbital. Transitions involving oxygen states can instead be viewed in terms of a single-particle picture.^{7,8}

The x-ray IPE line shape of Ref. 10 shows four features at 4, 9.5, 13.5, and 18 eV above E_F , respectively. In the UV IPE results of Ref. 17 two structures are visible at 3.7 eV and about 13 eV and the presence of a third peak at ~ 17 eV (not shown in the figures) is mentioned. The general inconsistency between the two IPE profiles is somewhat unexpected since they both refer to measurements integrated over k .²⁶

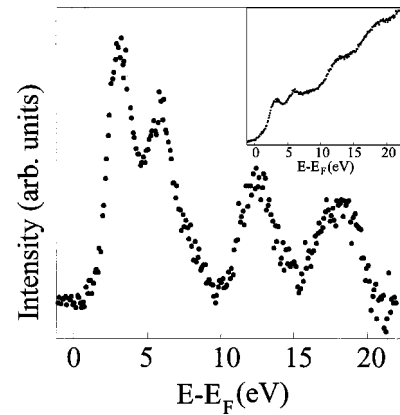


FIG. 1. IPE spectrum of NiO(100) grown on a Ag(100) substrate after the subtraction of a linear background (in the form of two straight lines with different slopes for the 0–10- and 10–20-eV range, respectively). Inset: NiO(100) IPE raw data.

While both papers attribute the peak closer to E_F to a d^9 final state they largely disagree on the $d^{10}L$ feature which is placed at 18 eV in Ref. 10 and at 13 eV in Ref. 17. Such a large indetermination influences considerably the present estimates of the excitation energies. The two features at 9.5 and 13.5 eV in Ref. 10 are attributed to $4s$ and $4p$ Ni bands, respectively, and are completely absent from Ref. 17 where a “ $d^8 4s$ ” label is placed at about 7 eV, which has no experimental counterpart in the spectral line shape.

The result of our IPE analysis on a 30-ML-thick NiO(100) film is reported, after a linear background subtraction, in the line shape of Fig. 1 for a normal incidence geometry. The spectrum in the inset shows the raw data. Four features are here clearly present, qualitatively similar to the result of Ref. 10. They can be better located using the background subtracted profile and are found to lie at 3.1, 5.8, 12.4, and 18.1 eV above E_F , respectively. Note that different choices of the background shape do not appreciably influence the peak energies. By analogy to previous studies^{10,17} an assignment of the peak closer to E_F as d^9 can be made while a statement on which is the $d^{10}L$ emission is much more ambiguous since both the 12.4-eV and the 18.1-eV structures seem to be possible candidates, as based on the two different previous claims.^{10,17}

In order to solve this problem the k dependence of the IPE peaks can be exploited: it is well known,^{3,11} in fact, that while Ni $3d$ states show a very small dispersion the s - and p -derived contributions are expected to depend largely on k . We have therefore collected IPE spectra at off-normal incidence, moving along the $\bar{\Gamma X}$ symmetry line up to 21° which roughly corresponds to the Brillouin-zone boundary. The results of such an analysis are shown in Fig. 2 after a background subtraction, similar to that used in Fig. 1. Moving from E_F , an analysis of these data clearly shows that while the first and third peaks keep a fixed energy (3.1 and 12.4 eV, respectively) the other two features display a sizeable dispersion. In this way the d^9 character of the 3.1-eV feature is confirmed and, more important, an assignment of the 12.4 eV as mainly $d^{10}L$ can definitely be established. Consequently it may be stated that the structures lying at 5.8 and 18.1 eV at

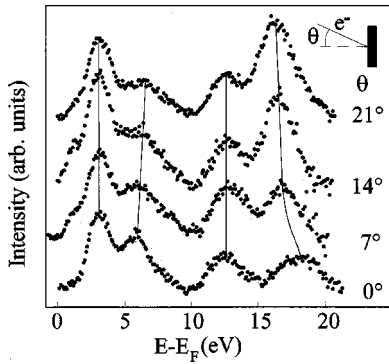


FIG. 2. IPE profiles taken at different incident angles as indicated in the inset. Normalization to the maximum intensity and background subtraction, as in Fig. 1, have been done. The dashed lines give an indication of the dispersion behavior for each peak.

normal incidence have basically a Ni $4sp$ band character. Some comments can now be drawn:

(i) In the assignments by Sawatzky and Allen¹⁰ an inversion of the $d^{10}L$ and $4p$ contributions takes places. The $d^{10}L$ feature is thus incorrectly assigned to the highest energy peak at ~ 18 eV. This results in a large (~ 5 eV) decrease of the d^9 to $d^{10}L$ separation which is in fact about 9 eV and calls for a reassessment of some previous fits²⁰ concerning the values of U and Δ . This separation is instead similar to what indicated by Hübner *et al.*¹⁷ and found by some of us on an oxidized Ni sample.²⁷

(ii) The recent successes obtained by so-called LDA+ U methods in getting a reasonable gap magnitude for NiO (Refs. 7 and 8) unfortunately do not help much to give a comparison with our results, at present: in Ref. 7 all the features found at larger energies than that of the d^9 contribution are assigned to Ni $4s$ and $4p$ derived bands and, surprisingly, apart from the d^9 feature, no mention of a further d -like intensity at higher energy is made, up to 20 eV above E_F ; in Ref. 8 the energy window goes only up to 5 eV above E_F and therefore everything but the d^9 structure is truncated.

(iii) As for the Ni $4s$ states, Ref. 17 fails to detect such a contribution (even if the above-mentioned label is correctly placed) whereas in Ref. 10 this is placed at higher energy with respect to our results, namely 2 eV larger than the maximum energy reached close to the zone boundary (i.e., ~ 7 eV at 21° off normal; see Fig. 2). In this case the comparison, though significant, cannot be completely conclusive since the information included in the x-ray IPE spectrum of Ref. 10 concerns the whole Brillouin zone and not only the ΓX symmetry line as in our data.

An analysis of the occupied electron states has been carried out as well by means of X-ray valence-band PE on the same NiO(100) surface as for the IPE results. In order to give a complete picture of the NiO spectral function a summary of these results is shown in Fig. 3. Three features, two peaks and one shoulder, are seen in the PE profile at about 2.6, 9.3, and 5.6 eV below E_F , respectively. In analogy to previous findings,^{3,10-12,17} they are attributed to d^8L , d^7 , and O $2p$ final states, respectively. It is worth noting that the energy separation found between the PE d^8L and the IPE d^9 peaks

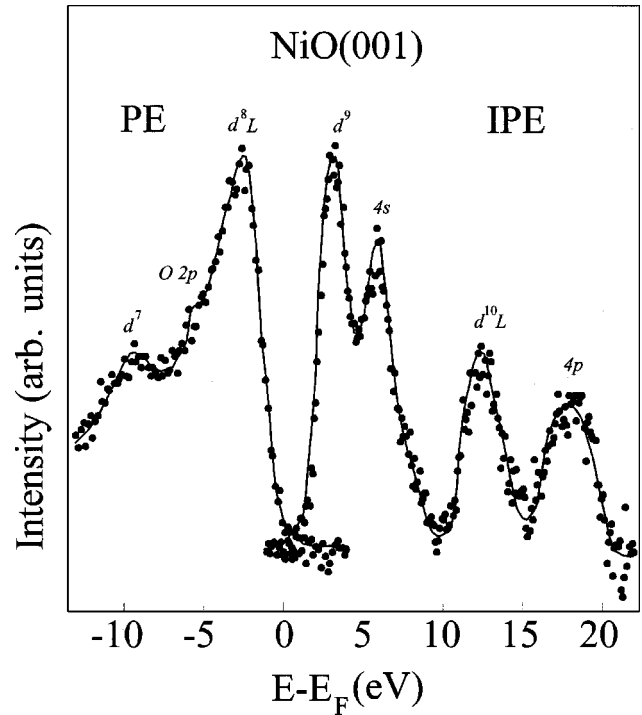


FIG. 3. Combined PE-IPE results around E_F . Spectra are arbitrarily normalized to their maximum intensity. The line on the spectra is a guide for the eye. See text for the meaning of labels.

is 5.7 eV, i.e., the same as for previously reported results.^{10,17,20} This separation is strictly related to the energy difference between the first ionization (for PE) and the first affinity (for IPE) state. As a consequence, whatever the criterion used to define the gap,²⁸ the same value is found in all cases. The invariance of the gap magnitude for samples obtained by means of different methods is not really surprising if we consider that this figure mainly depends upon bulk properties more than surface quality in terms, e.g., of roughness, defects, etc. Moreover, the previous results^{10,12,17} showed a pinning of E_F close to the d^8L peak (about 2 eV apart). This occurrence made previous reports (see, e.g., Ref. 3) to state that “hole” doping is always present in NiO since this is a defect material with metal vacancies and to give some interpretations for the Fermi level pinning in “pure” NiO. However, more recent UV PE results obtained from NiO(100) thin films grown onto Ag(100) (Ref. 22) show a shift of the d^8L intensity away from E_F of about 0.5 eV with respect to PE results collected with the same photon energy for cleaved NiO(100) crystals.¹² A similar shift is found in the present work with respect to previous XPS reports.^{10,20} As a result it can be generalized that the position of E_F is nearly centered inside the gap when NiO(100) is grown on top of Ag(100) at variance with the case of a (100) surface obtained by cleaving a NiO single crystal. If we attempt to draw some information concerning the presence of defects in these structures we could infer that the acceptorlike defects present in cleaved NiO(100), which are responsible for the mentioned pinning of E_F , are not present in the grown thin films. In fact, a compensation of these defects by means of donorlike defects would give clear features close to E_F , de-

tected both by PE (Ref. 12) and IPE (Ref. 20). Since these are absent in our results, we can suggest that the microscopic structure of the NiO(100)/Ag(100) thin films is closer to the ideal NiO in terms of defects with respect to the case of cleaved NiO single crystals, in agreement with a scanning tunneling microscopy study performed on the NiO(100) thin films.²² As a consequence the formation of a nearly intrinsic electron structure seems to take place.

In conclusion, we have performed a detailed IPE study on NiO(100) thin films grown on a Ag(100) substrate. We have shown that four structures are present in the spectra and were able to understand their orbital character by means of a **k**-resolved analysis. In particular it was possible to locate the position of the $d^{10}L$ ligand hole state which was largely misplaced in previous reports with consequences on the results

of model calculations. Combining these results to valence-band PE data taken on the same surface the complete spectral function has been obtained. At variance with the results on cleaved NiO(100) single crystals where the Fermi level is strongly pinned close to the valence-band maximum, we showed that the position of E_F is placed close to midgap, likely indicating the formation of a NiO phase closer to the ideal one than those obtained by bulk single crystals in terms of defect structure.

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- ²⁶In Ref. 10 this is due to the high photon energy, while in Ref. 17 it is due to the polycrystalline nature of the sample.
- ²⁷L. Duò and L. Braicovich (unpublished). In this case the photon energy dependence (in the 10–25-eV range) of the IPE spectral weight in terms of the cross section clearly indicates the d nature of both the features labeled as d^9 and $d^{10}L$.
- ²⁸In Ref. 3 it is thoroughly discussed as, using the same data set, it is possible to obtain largely different values of the gap magnitude according to the method adopted to define it. In all cases, once the method is established this value depends only upon the d^8L - d^9 energy difference and the gap edges turn out to be centered with respect to the these peaks.