Growth of NiO on Ag(001): Atomic Environment, Strain, and Interface Relaxations Studied by Polarization Dependent Extended X-ray Absorption Fine Structure

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This paper reports a structural study of 3 and 10 monolayer (ML) thick NiO films grown on Ag(001). Polarization-dependent X-ray absorption spectroscopy at the Ni K edge allowed us to obtain an accurate description of the local atomic environment of the Ni atoms up to the seventh coordination shell, including the determination of the in-plane and out-of-plane strains for the NiO films (determined with an accuracy better than 1%, resulting from the determination of Ni–O bond distances with a statistical error lower than 0.01 Å). Multishell multiple scattering calculations have been used to fit the data. Within the experimental errors, the 3 ML film has both in and out-of-plane Ni–O distances compatible with those expected in the case of perfect pseudomorphism on Ag(001). A rough film morphology, possibly including also the presence of NiO islands, is also suggested by the optimized coordination numbers. Conversely the 10 ML film is partially relaxed without significant deviation from ideal bidimensional film. The present EXAFS study allows us to rule out any significant atomic interdiffusion process between the substrate and the NiO film. Comparison with previous literature data allows us to make the hypothesis of a two step growth mechanism for NiO films on Ag(001). The NiO–Ag(001) interface distance determined in this EXAFS study ($d_{interface} = 2.36 \pm 0.05$ Å) is in remarkable agreement with theoretical calculations ($d_{interface} = 2.38$ Å).

1. Introduction

Few monolayer (ML) thick NiO and MgO films on Ag(001) exhibit a surprising chemical reactivity with a high degree of chemical specificity and the sticking coefficient for H_2O chemisorption, which is close to unity.¹ This has been suggested to be due to the presence of hybridized states with strong O 2p character, which are pushed close to and above the Fermi level due to the mixing with the substrate Ag 5sp states, in an energy region within the bulk oxide band gap. The confirmation of this scenario would imply that, because of hybridization effects, oxide—metal interfaces have unprecedented chemical properties.

However, the high hydroxylation rate observed for MgO and NiO films on Ag(100) might also be caused by the intrinsic crystal structure of the oxide thin film. In fact, it is by now generally recognized that the chemical activity of oxide surfaces is strongly determined by the coordination number and the oxygen-cation bond length, so that, for example, low coordinated step edges and corners are preferential sites for very efficient chemisorption processes performed on single crystals, thin films, and powdered systems.^{2–7}

Of particular relevance in the understanding of several fundamental phenomena has been the study of the interaction of H₂O with NiO and parent MgO oxide surfaces.^{2,8-12} Reissner et al. reported that the H₂O uptake on thin NiO films grown on Ag(001) increases with increasing surface defectivity.¹¹ H₂O undergoes heterolytic dissociation, through a nucleophilic attack by the basic O²⁻ anions; hence, the MgO surface becomes immediately covered by a full layer of hydroxyl groups, as demonstrated by some IR investigations.¹³ In this regard also, the contributions of Echterhoff et al.¹⁴ and Knözinger et al.¹⁵ together with some theoretical contribution¹⁶⁻²¹ should be noted. Among them, Scamehorn et al.¹⁸ report two stable configurations for H₂O molecules physisorbed on MgO(001): H₂O either forms a bifurcate hydrogen bond with the O²⁻ ions of the surface or an oxygen down configuration on top of the Mg²⁺ cation. Xu and Goodman²² reported a combined TPD, IRAS, and LEED study on D₂O adsorbed on thin MgO(001) films grown on a Mo(001) substrate. As far as experiments on MgO(001) single crystals are concerned, elastic helium scattering and LEED investigations were carried out by Ferry et al.23,24 and a

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combined LEED and IR study (with polarized IR source) was reported by Heidberg et al.²⁵ The hydroxyl groups formed on low coordinated sites of MgO(001) after dissociative adsorption of water have been characterized with high-resolution EELS by Xu et al.²⁶ and by Coustet and Jupille in a combined highresolution EELS and XPS study.²⁷⁻²⁹ Of particular relevance for the present work is the thickness-dependent investigation of the strain in MgO films (1-20 ML) pseudomorphically grown on Ag(001).³⁰ The final picture emerging from all these studies is that, on both NiO and MgO surfaces, regular five coordinated sites are not able to dissociate H₂O and that the process occurs on four and three coordinated sites only. The reactivity of NiO films on Ag(001) toward potassium has been studied using ultraviolet photoelectron spectroscopy (UPS), X-ray photoelectron spectroscopy (XPS), and low energy electron diffraction (LEED).³¹

From this picture, it is clear that any modification of the bond length and of the coordination number due to lattice deformations associated with the lattice misfit of the oxide with the substrate can significantly influence the chemical properties of the oxide thin film. For this reason, the choice of a substrate with a lattice parameter very similar to that of the film and with the same crystallographic structure is of fundamental importance. The lattice parameter of Ag is sufficiently close to that of NiO and MgO, yielding misfits of 2.2% and 3%, respectively; furthermore, the speed of Ag oxidation is lower than that of Ni or Mg and this prevents the substrate oxidation and consequent structural changes.

Ultrathin NiO films grown on Ag(001) present also interesting magnetic properties^{32,33} different from the bulk.³⁴ Their structure has been studied with different techniques, such as Auger electron diffraction,³⁵ photoelectron diffraction,³⁶ primary beam diffraction modulated electron emission (PDMEE),³⁷ LEED,³⁷⁻³⁹ electron energy loss,³⁹ and direct^{31,40} and inverse⁴⁰ electron photoemission spectroscopies. The films are found to be pseudomorphic to Ag up to a thickness of \sim 5 ML. For higher coverages, the strain is suggested to be released by the introduction of misfit dislocations.³⁸ XPS has been used by Luches et al.³⁶ and by Reissner et al.,^{10,11} the latter group having also reported an ultraviolet photoelectron spectroscopy study. The film morphology has been investigated by means of STM,^{41,42} which suggested a rather complex interface with NiO island formation and the presence of vacancy islands in the Ag substrate after NiO deposition.

In this work, we have used extended X-ray absorption fine structure (EXAFS) to determine the local atomic environment of Ni within thin oxide films pseudomorphically grown on Ag(001) substrate. The good quality of the EXAFS data allows us to perform the data analysis by including up to the 7th coordination shell around Ni. This result represents a strong improvement with respect to a preliminary analysis performed up to the third coordination shell only.⁴³ In this work, we have determined the variation of interatomic distances induced by strain and the epilayer-substrate atomic correlations with remarkably low statistical errors. EXAFS is a powerful tool for local structural determination, which has been used to study surface and interface structure.44 The use of third generation synchrotron radiation sources, coupled to state of the art beamlines and experimental setups allows us to obtain data of high quality even on few ML-thin epilayers. The polarization dependence of the EXAFS cross section allows structural determination with directional sensitivity; in fact, by exploiting the linear polarization of the synchrotron beam and by orienting the sample with the surface normal either parallel or perpendicular to the electric vector of the impinging radiation, it is possible to preferentially probe out-of-plane or in-plane atomic correlations. For example, the technique has been recently used to directionally probe distortions of the local structure induced by heteroepitaxial growth in cubic semiconductor alloys⁴⁵ and in hexagonal nitrides.⁴⁶ The sensitivity to small strain-induced variations in bond lengths has been demonstrated for InGaAs on InP.^{47,48} The ability of EXAFS to detect atomic interdiffusion processes at interfaces is illustrated by work on Ge dots on Si.⁴⁹ In the field of oxides, EXAFS has been used to probe the local structure in magnetron-sputtered NiO films⁵⁰ and to determine the adsorption site of Ag on MgO.⁵¹

2. Experimental Section

2.1. Sample Preparation. The samples used for the present study are two ex situ grown NiO films on Ag(001) single crystals 3 and 10 ML thick. The films were protected by a capping layer of 5 ML of MgO to prevent hydroxylation of the NiO film surface. Given the small lattice parameter mismatch between NiO and MgO (0.8%), the possible modifications of the structure induced by the capping layer are expected to be negligible. It is so assumed that the local structure of ex situ, MgO-capped, NiO/Ag(001) films is virtually equivalent to that of in situ NiO/Ag(001) films. The Ag(001) substrate was cleaned by repeated cycles of sputtering (0.6 keV, 1μ A/cm²) and annealing (700 K) in UHV. The evaporation rates were measured by means of a quartz crystal microbalance. Both NiO films and MgO capping layers were grown using Knudsen cells and a directional O₂ flux on the sample resulting in a background oxygen pressure of 7×10^{-8} Torr in the growth chamber. The rate of oxide formation was approximately 1 ML/min, as evaluated by the deposition rates and the relative Ni (Mg) density in metallic Ni (Mg) and in NiO (MgO). The Ag substrate was kept at 460 K during film growth. In the following, we shall express the film thickness in monolayers (ML), where 1 ML corresponds to a number of atoms/cm² equal to the surface density of atoms in bulk NiO (1.15 10¹⁵ Ni and O atoms/cm²).

A sintered bulk NiO sample was measured as a reference. Nickel hydroxide powder, sintered at 900 °C, was used as a precursor of NiO. The resulting NiO is highly sintered and is characterized by many cubic or prismatic microcrystals prevalently exposing (100) and (111) planes and with dimension in the range of 500–2000 Å.⁵

2.2. Data Collection. The EXAFS measurements were performed at the GILDA beamline, at the European Synchrotron Radiation Facility (Grenoble, France). The photon energy in the Ni K edge range was obtained by means of a double crystal monochromator used in dynamical focusing mode.⁵² The EXAFS spectra of the films were recorded in the fluorescence mode using a 13 elements hyper-pure Ge detector, whereas the sintered NiO sample was measured in the transmission mode.

Being the synchrotron radiation linearly polarized in the plane of the electron orbit, the substrate Ag(001) single crystal can be oriented in the electric field (**E**) of the photon beam in order to modulate the angle θ between the growth axis and **E** ideally in the 0–90° range. To discuss the expected polarization dependence of the spectra, we will use the approximation in which each two-body atomic correlation contributes to the total signal with a weight equal to $\cos^2(\alpha)$ where α is the angle between the interatomic vector **r** and the electric vector **E**. This approximation is valid within the plane wave and small atom limits and, in fact, has not been adopted in the data analysis;



Figure 1. Representation of the portion of the NiO cluster adopted for the FEFF calculation lying in the positive region of the *x*, *y*, and *z* axes. Small spheres represent the Ni, whereas the big ones refer to O. Number 0 identifies the absorbing Ni atom, whereas the progressive 1-7 numbers refer to the 1st-7th coordination shell around Ni(0). All atoms belonging to the same shell are degenerate in the cubic symmetry of the bulk case and so do the scattering paths. The letters following the numbers are used to distinguish atoms of the same shell once the degeneration is removed by tetragonal distortion.

however, it does provide the major polarization dependence and is thus useful for the sake of a qualitative discussion. As a consequence, a modulation in θ implies a modulation in $\cos^2(\alpha)$, i.e., in the relative weight between in-plane and out-of-plane distances of the pseudomorphic film. In the ideal cases of $\theta =$ 0 and 90°, only one contribution is present. For practical reasons the $\theta = 90^{\circ}$ and 0° limit cases cannot be reached. For the films, we used two different scattering geometries at $\theta = 75^{\circ}$ and 15°, to be selectively sensitive to in-plane and out-of-plane structures respectively, hereafter labeled as normal and grazing incidence. In such cases, the mixing with the undesired contribution is, within the plane wave approximation, equal to $\cos^2(15^\circ)$, i.e., less than 7%, which can be considered as negligible in the EXAFS data analysis. To allow the simultaneous determination of both in-plane and out-of-plane distances also a geometry with $\theta = 45^{\circ}$ has been used.

2.3. EXAFS Data Analysis. Nickel oxide, which has the rock-salt structure with the Ni ions forming a face-centeredcubic (rocksalt, see Figure 1) lattice, is an example of compound where multiple scattering is expected to be strong because of the presence of forward-scattering paths consisting of collinear arrangements of neighboring atoms (also called focusing effects).53,54 The importance of the MS contributions in the EXAFS data of rock-salt oxides has clearly been evidenced in previous papers reporting EXAFS studies on both NiO55 and MgO⁵⁶ polycrystalline powders and on NiO films on polymide film substrate.50 For this reason, data analysis was carried out using the FEFF 8.10 code57 where the effect of multiple scattering can be included by calculating all single and multiple scattering paths, starting and ending on the absorbing atom, within a total path length shorter than a cutoff threshold $(2R_{\text{cut-off}})$. For single scattering paths, the total path length is simply twice the distance between the absorbing and the scattering atoms, i.e., twice the distance of the *i*th coordination shell (hereafter R_i). To allow a direct comparison between scattering path lengths and atomic distances, FEFF 8.10 orders the different paths as a function of R_{path} , defined as the half of the total path length. In such a way, for all single scattering paths, R_{path} will coincide with the corresponding R_i .

Because the number of paths $N_{\text{path}}(R_{\text{cut-off}})$ rapidly diverges with $R_{\text{cut-off}}$, $[N_{\text{path}}(3 \text{ Å}) = 2$, $N_{\text{path}}(4 \text{ Å}) = 5$, $N_{\text{path}}(5 \text{ Å}) = 21$, $N_{\text{path}}(6 \text{ Å}) = 75$ for bulk NiO], a discrimination method must be applied to limit the number of paths included in the simulations. The adopted method is based on the evaluation of the integration, in *k* space, of the amplitude function of each path (*A*). The value of the *A* integral of the first-shell single scattering contribution is arbitrarily set to 100 and all remaining *A* values scale in a proportional way. All paths having an *A* value higher than 10 or lower than 5 have been included or ignored in a straightforward manner. For all paths having $5 \le A \le 10$, a manual choice has been done depending on the *k* and *R* regions where they give their main contribution. It is worth noticing that, in the particular case of oxygen and nickel atoms, which are separated in the periodic table by 20 elements, the maxima of the respective scattering amplitudes are shifted in *k* space by $\sim 4 \text{ Å}^{-1}$, so that the oxygen and nickel atoms contribute mainly in the $1-6 \text{ Å}^{-1}$ and $5-15 \text{ Å}^{-1}$ ranges, respectively.

The data processing was performed through five subsequent steps. (i) The $\chi(k)$ function has been extracted from the raw absorption data using AutoBK58 program. (ii) A structural model of the reference compound (NiO bulk) was constructed using the ATOMS program.⁵⁹ (iii) Theoretical phase shifts and amplitudes, for the paths satisfying the $R_{\text{path}} \leq R_{\text{cut-off}}$ relationship, were generated by means of FEFF 8.10 code⁵⁷ on the basis of the NiO rock-salt structure; the polarization was explicitly taken into account (vide infra) when generating the theoretical signal. (iv) For the reference sample (sintered NiO), the experimental EXAFS signal was fitted with the theoretical one, using the FEFFIT 2.55 program.⁶⁰ This allowed us to determine the most significant multiple scattering paths and the S_0^2 factor (superposition integral of the passive electrons wave functions) and to verify the ability of the adopted phases and amplitudes to reproduce the structure known by diffraction data. (v) On the basis of the results obtained for the reference sample, data fitting of the EXAFS signal was performed for the films also.

The model $\chi(k)$ used to compare to data is evaluated as a sum over all selected paths and depends on the scattering amplitudes and phase-shifts and on the standard EXAFS parameters (coordination number, change in distance, Debye– Waller Factors) of each path and on a unique shift in energy origin, common to all paths. The EXAFS contribution of each selected scattering path is adjusted by optimizing the abovementioned parameters until the best fit to the data is found.

Coming to the analysis of the reference sample (sintered NiO), an $R_{\text{cut-off}} = 6$ Å was adopted. Within this value, 14 different scattering paths (see the Appendix) were considered to simulate the theoretical EXAFS signal, each one weighted by the corresponding degeneration factor (6 for the 1st shell SS, 12 for the 2nd shell SS, and so on), automatically computed by the FEFF code. As described above, the standard EXAFS parameters are a single S_0^2 factor and a single energy (ΔE) shift (common to all paths), the Debye–Waller factors (σ_i), the coordination numbers (N_i) , and the change in distances (ΔR_i) with respect to an initial R_i guess). This results in a huge number of parameters for 14 different paths. To minimize the number of optimized fitting parameters we have fixed the coordination numbers to the values expected for a rocksalt structure and all 14 path length variations ΔR_i have been expressed as a function of a single parameter β , representing the isotropic volume expansion (contraction if $\beta < 1$) coefficient. It is so assumed that the NiO cluster undergoes an isotropic expansion; i.e., the distances along all three axes expand or contract by the same constant of proportionality. In such a way, for all paths the optimized path length can be expressed as the product αR_{path}^0 , being R_{path}^0 the initial guess given by XRD. In such approach, the total number of optimized parameters is reduced to 13: (i) one S_0^2 ; (ii) one ΔE ; (iii) one β ; and (iv) 10 σ_i factors. Note

that σ_i factors have been independently optimized for the seven SS paths, whereas for the MS paths, we have fitted independently only those related to the two collinear paths contributing in the 4th shell region. A single Debye–Waller factor was considered for the four MS paths contributing in the 7th shell region.

Coming to the films analysis, the polarization of the synchrotron beam (i.e., the direction of the electric field E of the incident beam) was explicitly taken into account. Assuming the z axis as the film growth axis and θ as the angle between z and **E**, hereafter, we will use the following correspondence between polarization direction and incidence geometry: polarization along [100] \leftrightarrow normal beam incidence ($\theta = 75^{\circ}$), polarization along [001] \Leftrightarrow grazing beam incidence ($\theta = 15^{\circ}$), polarization along [101] \Leftrightarrow 45° incidence (θ = 45°). The introduction of the polarization removes the degeneration of several scattering paths. As a consequence, the number of paths within $R_{\text{cut-off}} = 6$ Å increases from 75 to, in the case of [100] polarization as an example, 167. In the Appendix, the case of polarization along the [100] direction is reported in detail as an example. The paths considered to simulate the theoretical EXAFS signal of the films were almost the same used for the reference sample. However, in this case, we must distinguish between the in-plane and out-of-plane contributions because of the different interatomic distances in the two directions (see Figure 1 and the Appendix for the [100] polarization case).

Regarding the fitting parameters, a separate discussion has to be done for the signal amplitude and the interatomic distances. The EXAFS signal amplitude depends essentially on the S_0^2 , the Debye-Waller factors, and the coordination numbers, for which the following choices were done. (i) Being S_0^2 exclusively a function of the absorbing atom, it was fixed at the value obtained for the reference sample. (ii) The Debye-Waller factors of all of the selected scattering paths were fitted starting from the values obtained for the reference sample; for the MS paths, we have adopted the same strategy as for the reference sample. (iii) Only the coordination numbers of the 1st and 2nd shells were fitted, because of the necessity of minimizing the fitting parameters; the remaining coordination numbers were fixed at the values expected for a rocksalt structure in the case of the 10 ML film and were multiplied by a scaling factor xconstant for all of the shells in the case of the 3 ML film measured at normal incidence.

Coming to the distances, the fits of the films data were performed on the hypothesis of an ideal tetragonal distortion; that is, all of the in-plane and out-of-plane distances are contracted/extended in the same proportion. On these bases, we have expressed all of the changes in interatomic distances with respect to the bulk case in terms of variations of the in-plane (ΔR_{\parallel}) and out-of-plane (ΔR_{\perp}) Ni-O bond distance (half of the lattice parameter, see the Appendix for the [100] polarization case). With the NiO lattice parameter being less than the Ag one, we expect a compression of the in-plane distances $(\Delta R_{\perp} > 0)$.

3. Results

3.1. EXAFS Data Analysis of the NiO Bulk Reference Material. Figure 2 (top) shows the magnitude of the phase uncorrected Fourier transform (FT) of the $k^3\chi(k)$ of the reference sample, both for experimental data (points) and for the best fit (solid line). The fit was performed in *R* space in the 1.0–6.0 Å range (evidenced by the white region in the figure), to take into account all the contributions until the 7th coordination shell. The FT was calculated in the range 2.5–15 Å⁻¹, with a k^3



Figure 2. Vertically shifted for clarity, from top to bottom the k^3 -weighted, phase uncorrected, FT of the $\chi(k)$ of experimental (points) superimposed with the best fit up to the 7th coordination shell (solid line); 1st shell SS; 2nd shell SS; 3rd shell SS; 4th shell SS; Ni(0)– O(1a)–Ni(4a)–Ni(0) MS path; Ni(0)–O(1a)–Ni(4a)–O(1a)–Ni(0) MS path; 5th shell SS; Ni(0)–O(1a)–O(5a)–Ni(0); 6th shell SS; 7th shell SS; Ni(0)–Ni(2a)–Ni(0) MS path; for the path definition. White and gray-dashed parts differentiate the *R* region where the experimental data have been fitted to those excluded from the fitting procedure.

weight to emphasize the high wavenumber part of the spectrum. In the bottom part of Figure 2, the single contributions of all of the SS and MS paths taken into account during the fit are also shown, vertically shifted for clarity. The experimental curve is characterized by five dominant peaks. By comparing the experimental curve with the single path contributions, the following considerations can be drawn (quoted distances are phase uncorrected). The peak around 1.7 Å is due to the first shell Ni–O atomic correlation, whereas the peak at \sim 2.6 Å is mainly due to the second shell Ni-Ni one. The higher distances peaks around 3.8, 4.7, and 5.5 Å result from the superimposition of several contributes but are basically centered where the 4th, 6th, and 7th coordination shells (Ni scatterers in all three cases) occur. The peaks relative to the 3rd and 5th coordination shells are not resolved due to the low backscattering amplitude of O compared to Ni (vide supra): corresponding contributions appear in the minimum of the experimental FT between the 2nd and 3rd and between 3rd and 4th peaks. The obtained β (1.002 ± 0.002) value results in a Ni–O first shell distance of $R = 2.092 \pm 0.004$ Å, to be compared with a value of 2.088 obtained from XRD. This datum, together with the obtained R_{factor} (0.037), confirms the validity of the choice of the scattering paths previously discussed and the accuracy of the corresponding phases and amplitudes functions computed by FEFF8.10 code. On the basis of these results, we have extended the fitting model to the films.

3.2. EXAFS Data Analysis of the NiO/Ag(001) Films. The raw EXAFS data are reported in Figure 3a. The six spectra collected in the fluorescence mode are of remarkable quality



Figure 3. Part a: Raw $k\chi(k)$ data of, from top to bottom: NiO sintered, 10 ML ($\theta = 75^{\circ}$); 10 ML ($\theta = 45^{\circ}$); 10 ML ($\theta = 15^{\circ}$); 3 ML ($\theta = 75^{\circ}$); 3 ML ($\theta = 45^{\circ}$); 3 ML ($\theta = 15^{\circ}$). Part b: First shell contributions as reported by the modulus of the k^3 -weighted, phase uncorrected, FTs of the data shown in part a of 10 ML ($\theta = 75^{\circ}$) and sintered NiO (dotted and full lines, respectively). The amplitude of the FT of the film has been multiplied by an arbitrary factor to result in a first shell signal of the same magnitude as the reference sample.



Figure 4. Comparison between experimental (points) and best fit (solid line) for the modulus of the k^3 -weighted, phase uncorrected, FTs of the experimental $\chi(k)$ of 10 ML ($\theta = 75^{\circ}$), 10 ML ($\theta = 15^{\circ}$), and 3 ML ($\theta = 75^{\circ}$), vertically shifted for clarity. Only signals from the tetragonally distorted NiO film contribute to the fit. See Tables 1 and 2 for the quantitative results extracted from these fits. White and gray-dashed parts as in Figure 2.

by considering that they have been collected on 3 and 10 ML thick films, corresponding to $\sim 3.45 \times 10^{15}$ and $\sim 1.15 \times 10^{16}$ Ni atoms cm⁻². In all fluorescence spectra, the oscillations and the main beats of the $k\chi(k)$ of the sintered NiO (measured in transmission mode, top spectrum) are visible up to 10 Å⁻¹ and in some cases up to 12 Å⁻¹. Such closeness with the fine structure of the model spectrum indicates that the local environment of Ni atoms in the films reflects the structure of NiO within several coordination shells (vide infra Figures 4 and 5 for the corresponding FTs).

The first coordination shell around Ni is the only one unaffected by MS contributions showing only in-plane and out-



Figure 5. Comparison between experimental (points) and best fit (solid line) for the modulus of the k^3 -weighted, phase uncorrected, FTs of the experimental $\chi(k)$ of 3 ML ($\theta = 15^\circ$). The upper curves refer to a fit including the signals from the tetragonally distorted NiO film only (i.e., with the same approach used in the fits reported in Figure 4). Bottom curves refer to the fit performed by including the 2nd shell Ni–Mg signal from MgO cap (dotted line) and the 2nd shell Ni–Ag signal from the Ag substrate (dashed line). White and gray-dashed parts as in Figure 2.

of-plane SS paths. It is so the best candidate to observe, on a qualitative ground, the presence of tetragonal strain. In the case of the film measured at normal incidence, a shift toward lower R is evident for the first shell contribution, reflecting a contraction of the in-plane Ni–O bond length ($R_{\rm II}$), as expected from pseudomorphism on a substrate with smaller lattice parameter (Figure 3b). Conversely, the R region where the first shell peak of the sample measured at grazing incidence appears is almost similar to that of the reference sample. We are so unable to estimate, on a qualitative ground (i.e., from a simple inspection of FT's), if the expected increase of the out-of-plane Ni–O bond length (R_{\perp}) occurs or not. To quantify the $R_{\rm II}$ contraction and to establish or confute the R_{\perp} elongation, a careful EXAFS data analysis must be carried out (see section 2.3).

The modulus of the k^3 -weighted, FTs of the experimental $\chi(k)$ for the 10 ML film, at normal and grazing incidence, and for the 3 ML film at normal incidence is shown in Figure 4 (points), superimposed to the best fit (solid line, vide infra for the optimization strategies). The fits were performed in R space in the 1.0–5.8 Å range for the 10 ML film (for both geometries) and in the 1.0-5.1 Å range for the 3 ML film (fit ranges are emphasized by the white region in the figure), to take into account all the contributions until the 7th and the 6th coordination shell, respectively. The FTs were calculated in the ranges 2.0–11.0 and 1.5–10.0 ${\rm \AA^{-1}}$ for the 10 and 3 ML films, respectively, with a k^3 weight. A qualitative comparison of the films FTs (Figure 4) with that of the reference sample (Figure 2, top) confirms that no major changes occur in the local environment of Ni in the epilayers; the only apparent change is a variation of the relative intensities of the different peaks, being that related to the second shell signal the most relevant one.

TABLE 1: In-Plane (R_{\parallel}) and Out-of-Plane (R_{\perp}) Ni–O First Shell Bond Lengths and Corresponding Strains $\epsilon_{\parallel} = (R_{\parallel} - R_0)/R_0$ and $\epsilon_{\perp} = (R_{\perp} - R_0)/R_0$ for the 3 and 10 ML Thick NiO/Ag(001) Films as Obtained from the EXAFS Data Analysis at Different Polarization Geometries^{*a*}

sample	θ	$R_{ }(\text{\AA})$	$\epsilon_{ }(\%)$	R_{\perp} (Å)	ϵ_{\perp} (%)
XRD		2.088	0	as $R_{ }$	as $\epsilon_{ }$
sintered		2.092 ± 0.004	$\pm 0.2 \pm 0.2$	as $R_{ }$	as $\epsilon_{ }$
10 ML	75	2.052 ± 0.006	-1.7 ± 0.3		
10 ML	15			2.101 ± 0.006	$\pm 0.6 \pm 0.3$
10 ML	45	2.062 ± 0.015	-1.2 ± 0.7	2.091 ± 0.024	$\pm 0 \pm 1$
3 ML	75	2.046 ± 0.009	-2.0 ± 0.4		
3 ML	15			2.12 ± 0.02	$+1.4 \pm 0.9$
3 ML	45	2.044 ± 0.009	-2.1 ± 0.4	2.133 ± 0.018	$\pm 2.1 \pm 0.9$

^{*a*} Experiments performed in normal (grazing) incidence are sensitive to the parallel (perpendicular) values only, whereas measures collected with $\theta = 45^{\circ}$ give information on both (although with higher incertitude). For comparison also, the unstrained Ni–O values obtained from XRD ($R_0 = 2.088$ Å) and from the EXAFS data analysis on the sintered NiO have been reported. See Figures 2, 4, and 5 for a view on the quality of the fits. The perfect pseudomorphism predicts $R_{\parallel} = \frac{1}{2a_{Ag(001)}}$, i.e., 2.045 Å.

 TABLE 2: Optimized First and Second Shell Coordination

 Numbers for the 3 and 10 ML Thick NiO/Ag(001) Films

 Measured at Normal and Grazing Geometries^a

	$N_{I}[100]$	$N_{I}[001]$	$N_2[100]$	$N_2[001]$
bulk theory	2	2	8	8
10 ML theory	2	1.8	8	7.2
10 ML	2	2.0 ± 0.6	8	7 ± 1
3ML theory	2	1.33	8	5.3
3 ML	2.8 ± 1.2	1.0 ± 0.2	6.1 ± 1.6	3.2 ± 0.9

^{*a*} Nonoptimized parameters can be evidenced by the absence of the relative error bars. For comparison, the "theory" lines report the values expected in the case of a perfect NiO tridimensional single crystal (bulk theory) and in the case of perfect bidimensional 10 and 3 ML thick NiO films. See Figures 4 and 5 for a view on the quality of the fits.

The data collected on the 10 ML film (at $\theta = 75^{\circ}$, 15°, and 45°, the latter not shown for brevity) have been satisfactorily optimized using R_{\parallel} and R_{\perp} as the unique structural parameters of the fit, being the coordination numbers fixed to those expected from a perfect NiO single crystal. This approach did not result in a satisfactory fit for the data collected on the 3 ML film for any polarization, reflecting the deviation from a perfect NiO single crystal, even if tetragonally distorted. For $\theta = 15^{\circ}$ and 45°, this deviation is expected to be due to the limited thickness of the film. The inability to fit the 3 ML ($\theta = 75^{\circ}$) data with fixed coordination numbers means that the film cannot be considered as a perfect bidimensional film and that the problem of surface roughness and of island formation must be considered. The direct observation of islands on the NiO layer surface has been indeed evidenced in the STM study of Sebastian et al.⁴¹

All data have so been subjected to new optimization cycles where the coordination numbers of the 1st and 2nd shell were fitted (hereafter N_1 and N_2). To minimize the number of fitting parameters, the coordination numbers of remaining shells and of MS paths were fixed at the values expected for a rocksalt structure multiplied by the scaling factor x constant for all of the shells. The results of these new optimization cycles are summarized for all cases in Tables 1 and 2 for bond distances and coordination numbers, respectively. In the 10 ML ($\theta = 75^{\circ}$) and 10 ML ($\theta = 45^{\circ}$) cases the introduction of N_1 and N_2 and x as fitting parameters does not improve the fit; for this reason, Tables 1 and 2 report the values obtained from the previous optimization cycles (N_1 and N_2 fixed, x = 1). For 10 ML ($\theta =$ 15°), a slightly improved fit was obtained resulting in a little decrement of N_2 and x values, which are however compatible with the single-crystal values within the error bars (note that N_1 was optimized exactly to the expected single-crystal value). Conversely, a strong improvement has been obtained for the 3 ML ($\theta = 75^{\circ}$) and 3 ML ($\theta = 45^{\circ}$), for which *x* was optimized to 0.7 \pm 0.1. Notwithstanding the use of variable N_1 and N_2 parameters, the optimization of the 3 ML ($\theta = 15^{\circ}$) signal still results incompatible with the experimental data.

It is finally worth noticing that the present EXAFS study allows to rule out any significant atomic interdiffusion process between the substrate and the NiO film, a kind of defectivity easily detected by EXAFS.⁴⁹

3.3. EXAFS Data Analysis of the 3 ML Thick NiO/Ag(001) Films with Beam Polarization in the [001] Direction. A different strategy must be used for the 3 ML film measured at grazing incidence. Notwithstanding the good quality of the experimental spectrum (bottom spectrum in Figure 3a), we were not able to perform a fit using the NiO contributions only (see Figure 5, upper curves). In fact, in grazing incidence geometry, we are sensitive to the out-of-plane distances so that we cannot ignore the contributions of the Ag substrate and of the MgO capping layer. Note that for the 10 ML thick sample such contributions have a much lower weight (1/20 instead of 1/6) and can be ignored.

According to the experimental results of Giovanardi et al.,68 to the theoretical calculation of Duffy et al.⁶² and of Casassa et al.33 for the NiO/Ag(001) system and in analogy with the MgO/ Ag(001) case,⁶³ we assumed that the oxygen atoms accommodate themselves on the substrate silver atoms. In the hypothesis of an ideal planar interface without interdiffusion, Ag atoms give rise to a 2nd shell contribution. This contribution has to be weighted for a 1/6 factor, because it represents half of the 2nd shell neighbors (the inferior ones) seen by 1/3 of the Ni atoms (those of the 1st ML). The SS Ni-Ag contribution to the EXAFS signal was simulated with a path generated by FEFF8.10 in the case of bulk NiO after substitution of the Ni 2nd shell atoms with Ag atoms. In such a way, the path is characterized by an initial Ni-Ag distance value equal to that of the Ni-Ni distance in bulk NiO which must be necessarily optimized during the fit.

Regarding the MgO capping layer, its influence could be in principle negligible, because of the small lattice mismatch between NiO and MgO (about 0.8%); nevertheless, we expect a deformation in the EXAFS signal because of the smaller scattering amplitude of Mg with respect to Ni. For this reason, we have simulated also the Mg contribution (again 2nd shell contribution) using the 2nd shell path generated by FEFF8.10 in the case of MgO with Ni as absorbing atom.

These two new contributions imply the following additional parameters to be optimized: $R_{\text{Ni}-\text{Ag}}$; $\sigma_{\text{Ni}-\text{Ag}}$; $\sigma_{\text{Mg}-\text{Ag}}$, being the coordination numbers fixed to those expected by $^{1/6}$ of second shell neighbors and being the $R_{\text{Ni}-\text{Mg}}$ distance optimized together with the second shell $R_{\text{Ni}-\text{Ni}}$. To limit the total number of fitting parameters, the following restrictions have been done on the basis of what learnt from the previous optimizations: (i) The shift in energy origin (ΔE) was fixed to the value obtained from the fit of the 3 ML ($\theta = 75^{\circ}$) and (ii) the variation of the inplane lattice parameter ΔR_{II} was fixed to the value expected in the case of a perfect pseudomorphism ($R_{\text{II}} = \frac{1}{2}a_{\text{Ag}(001)} = 2.045$ Å), a value compatible with that optimized in the 3 ML ($\theta = 75^{\circ}$) case, see Table 1.

In Figure 5 (lower curves), a comparison between experimental (points) and best fit (including substrate and cap contributions, solid line) for the modulus, FT of the experimental $k^3\chi(k)$ of the 3 ML film measured at grazing incidence is shown. The FT was calculated in the 1.5–10 Å⁻¹ range. The fit was performed in *R* space in the 1.0–3.5 Å range (evidenced by the white region of the Figure) to take into account all of the contributions until the 3rd coordination shell. In the picture also, the 2nd shell Ni–Mg signal from MgO cap (dotted line) and the 2nd shell Ni–Ag signal from the Ag substrate (dashed line) are specifically shown. The presence of the Ni–Ag contribution, occurring in a region where that of the NiO is absent, is mandatory to obtain a good fit (see upper curves in Figure 5). Also the introduction of the Ni–Mg contribution improves the fit, in the 2–3 Å region. We can so, a posteriori, understand the failure of the fits previously attempted. The structural parameters extracted from this fit are summarized in Tables 1 and 2, and the optimized Ni–Ag distance is of 3.13 ± 0.04 Å.

4. Discussion

4.1. Coordination Numbers. As previously discussed, a qualitative inspection of the experimental FTs reveals that the films spectra are very similar to that of NiO bulk (Figure 3a) and that the major change is a reduction in the amplitude of second shell signal with respect to the first shell one. This reflects a decrease of the 2nd shell neighbors with respect to the 1st shell ones, which is quantified in the data summarized in Table 2. It is clear that for the 10 ML film N_1 and N_2 values measured in both polarizations are compatible with a model of a perfectly bidimensionally flat film without roughness effects. Conversely, for the 3 ML film, only $N_1[100]$ fits the theoretical value within the experimental errors, being $N_2[100]$, $N_1[001]$, and $N_2[001]$ lower than the expected values. Comparing experimental and theoretical values, it is clear that the 10 ML film can be considered, within the EXAFS sensitivity, as structurally perfect. Instead, in the case of the 3 ML film, a great discrepancy with the expected values can be noted. This experimental evidence is in agreement with the hypothesis of an increasing roughness in surface morphology with decreasing film thickness, because of island formation at the first stages of the growth.41,42

4.2. Interatomic Distances. Figure 6 summarizes the outof-plane Ni-O distance as a function of the in-plane one, according with the values reported in Table 1. The open circle represents the unstrained bulk NiO ($R_{\parallel} = R_{\perp} = R_0 = 2.088$ Å) as determined by XRD, whereas the full circle represents the EXAFS value obtained from sintered NiO. The straight line is obtained following the elastic theory approximation, according to the equation $R_{\perp} = -\gamma R_{\parallel} + (1 + \gamma)R_0$, where the ratio γ is defined as $\gamma = 2C_{12}/C_{11}$ and C_{11} and C_{12} are the elastic stiffness constants of bulk NiO; values of $C_{11} = 344.6$ GPa and $C_{12} =$ 141 GPa⁶⁴ give $\gamma = 0.818$. The star represents the values expected for an ideal NiO layer in perfect pseudomorphism on Ag(001): $R_{\rm H} = 1/_2 a_{\rm Ag(001)} = 2.045$ Å and $R_{\perp} =$ 2.125 Å. The 10 ML (full triangle) and 3 ML (full square) positions have been represented using the R_{\parallel} and R_{\perp} values obtained from analysis of the normal and grazing incidence data, respectively. The $R_{\rm II}$ and R_{\perp} values obtained using the data collected at $\theta = 45^{\circ}$ are represented with open triangle and square for the 10 ML and the 3 ML film, respectively. On the basis of this picture three main considerations can be drawn.

(i) The values obtained fitting the data collected at incidence angle of 45° are perfectly consistent, within the experimental error, with those obtained from the combined analysis of the data collected at normal and grazing incidence, confirming the goodness of the model.

(ii) Both 10 and 3 ML films seem to be compressed in the growth plane, to fit the smaller Ag(001) substrate lattice constant. The 3 ML film presents R_{\parallel} and R_{\perp} values very similar



Figure 6. Out-of-plane Ni–O bond distance vs. in-plane one of thin NiO films: full square 3 ML ($\theta = 15^{\circ}$ and 75°), open square 3 ML ($\theta = 45^{\circ}$), full triangle 10 ML ($\theta = 15^{\circ}$ and 75°), open triangle 10 ML ($\theta = 45^{\circ}$) and full circle sintered NiO determined in this EXAFS study. Straight line represents the theoretical R_{\perp} vs R_{\parallel} relationship predicted by the elastic theory, adopting the Poisson ratio of the NiO bulk ($\gamma = 0.818$).⁷² Big dot represents the unstrained NiO bulk (XRD), and the star represents the ideal perfect pseudomorphism of NiO on Ag(001).

to those expected for a perfect pseudomorphism, whereas the 10 ML film appears partially relaxed along the growth direction. This suggests that the critical thickness for strain release lies between 3 and 10 ML. The in-plane contraction of the 10 ML film is in disagreement with the results of other works which, on the basis of electron scattering experiments, find a critical thickness for strain release of 5 ML.^{36,38} This difference can be understood on the basis of the different sampling depth of the different techniques. In the case of EXAFS spectra detected in fluorescence mode, the information comes from the whole thickness of the sample under study and allows to affirm that the most part of the atoms in the 10 ML film are still in an in-plane contracted local environment. Electron scattering techniques, instead, sample only the outermost film layers, which can be in a more relaxed environment. With the *R* values being obtained from EXAFS an average of the situation seen by Ni atoms in all layers, the combination of the present EXAFS results and the electron diffraction ones^{36,38} suggests a model where strain relaxation starts around 5-6 ML and affects only the subsequent layers, being the first 4-5 still under perfect pseudomorphism.

(iii) Marcus⁶⁵ has suggested that the Poisson ratio for thin films is different from the bulk one. An attempt to perform a linear fit on the experimental data reported in Figure 6 seems to support this thesis for the NiO system; however, the too limited number of experimental points and the relative large error bars prevent any definitive conclusion. Moreover, particularly for the 3 ML case, it must also be considered that the morphology of the system is possibly not two-dimensional but rather in the form of islands: in this case, the relation between in-plane and out-of-plane strain is not expected to be simply via the bulk Poisson ratio.

4.3. NiO-Ag(001) Interfacial Distance. It has been recently proposed that ultrathin oxide films and oxide-metal interfaces

may actually have unprecedented intrinsic chemical-physical properties, because of image potential screening of charge fluctuations and interfacial hybridizational effects.^{1,66,67} The presence of a metal substrate, where electrons can move freely, implies a consistent reduction in the energy cost to transfer one electron from the valence band (with mainly O2p character) to the conduction band (mainly centered on the cation), because of the formation of image charges on the metal at the metal/ oxide interface, resulting in a net reduction of the band gap. In the case of ultrathin layers (1 ML), even the insulating-metal transition has been inferred. Altieri et al.^{1,67} have demonstrated from X-ray photoemission spectroscopy and Auger electron spectroscopy experiments that the on-site Coulomb interaction (defined as the energy necessary to transfer an electron from a cation to another) and the charge-transfer energy (defined as the energy cost to transfer an electron from the anion to the cation) in thin MgO films becomes significantly smaller than in the bulk. The influence of the metal substrate on these physical quantities, strictly related to the band-gap width, can still be felt as far as 10 ML away from the interface. The demonstrated ability to control the film thickness represents therefore a new technological opportunity for band-gap engineering. For a given oxide/metal system, the structural parameter that establishes the $E_{\rm g}$ vs the film thickness relationship is the oxide/metal interface distance ($d_{interface}$). It is so evident that this parameter must be carefully determined in order to design a film with desired electronic characteristic. In principle, once $d_{\text{interface}}$ has been measured, the E_{g} vs the film thickness relationship is fixed, and so the latter can be ad hoc selected to yield the desired $E_{\rm g}$.

Regarding the Ag substrate contribution, the fit performed on the 3 ML film measured at grazing incidence (see bottom of Figure 5) gives a Ni–Ag distance of 3.13 ± 0.04 Å. In accord with the hypothesis of an interface in which the O atoms are located on top of Ag atoms and assuming a perfect pseudomorphic growth (i.e., a Ni-O distance at the interface equal to $1/2a_{Ag(001)}$, a value in agreement with the measured $R_{\parallel} = 2.044$ \pm 0.009 Å, see Table 1), we have calculated the interfacial distance between the Ag surface and the NiO layer as $d_{\text{interface}}$ = 2.37 ± 0.05 Å. This value is expanded if compared to both NiO and Ag half lattice parameters (2.088 and 2.045 Å, respectively) and is perfectly in agreement with that obtained with periodic ab initio calculation of Casassa et al.33 performed with CRYSTAL98 code on one monolayer of NiO on Ag $(d_{\text{interface}} = 2.38 \text{ Å})$ and with that measured by Giovanardi et al.⁶⁸ with PDMEE technique ($d_{\text{interface}} = 2.3 \pm 0.1 \text{ Å}$).

5. Conclusions

Polarization dependent EXAFS measurements and their multiple scattering multishell analysis, up to the 7th coordination shell, have allowed us a quantitative determination of the structure of ultrathin NiO films on Ag(001). We found that the local structure is the rock-salt one and that the intermixing with the Ag substrate is negligible at the atomic scale. The 3 ML film has both R_{\parallel} and R_{\perp} values compatible with those expected in the case of perfect pseudomorphism on Ag(001), within the experimental errors (0.009 and 0.02 Å respectively). Conversely, the 10 ML film is partially relaxed: in this case Ni-O bond distances have been determined with an accuracy of 0.006 Å for both polarizations. For the 3 ML film, a rough morphology, possibly including also the presence of NiO islands, is also suggested by the optimized coordination numbers. From a merge of all of the literature data and of the present EXAFS results, a two steps growth mechanism for NiO films on an Ag(001) substrate can be hypothesized. The first step is characterized by the nucleation of NiO crystallites perfectly matched with the substrate, starting from islands: this phase is characterized by a great surface roughness so that the $N_2[100]$, $N_1[001]$, and $N_2[001]$ values are lower than the expected ones. In the second step, occurring around 4-6 ML, the elastic energy stored during the distortion increases until it is partially released through the creation of dislocations. At the same time, the NiO islands grow and begin to connect together until the film grows in a completely relaxed manner showing, within the experimental errors, coordination numbers in agreement with the hypothesis of a perfect bidimensional film. The EXAFS data collected in grazing geometry on the 3 ML sample detected a significant Ni-Ag contribution which has allowed us to determine the NiO-Ag(001) interface distance: $d_{\text{interface}} = 2.37 \pm 0.06$ Å, a value in remarkable agreement with both theoretical³³ ($d_{interface}$ = 2.38 Å) and independent PDMEE experiments⁶⁸ ($d_{\text{interface}} =$ 2.3 ± 0.1 Å).

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TABLE 3:	Туре,	Degeneration	ı, and	Length	Variation,	Due to	Tetragonal	Distortion	of SS	Paths	Involved	in the	EXAFS	Data
Analysis of	the Fi	lms in the Ca	ase of	[100] Po	larization ^a									

paths	degeneration	path length variation
Ni(0) - O(1a) - Ni(0)	2	$\Delta R_1 = \Delta R_{ }$
Ni(0)-Ni(2a)-Ni(0)	4	$\Delta R_{2in} = \sqrt{2} \Delta R_{ }$
Ni(0)-Ni(2b)-Ni(0)	4	$\Delta R_{2\text{out}} = \sqrt{2R_1^2 + 2R_1(\Delta R_{11} + \Delta R_{12}) + \Delta R_{11}^2 + \Delta R_{12}^2} - \sqrt{2}R_1$
Ni(0)-O(3)-Ni(0)	8	$\Delta R_{3} = \sqrt{3R_{1}^{2} + 2R_{1}(2\Delta R_{\parallel} + \Delta R_{\perp}) + 2\Delta R_{\parallel}^{2} + \Delta R_{\perp}^{2}} - \sqrt{3}R_{1}$
Ni(0)-Ni(4a)-Ni(0)	2	$\Delta R_4 = 2\Delta R_{\parallel}$
Ni(0)-O(5a)-Ni(0) and Ni(0)-O(5b)-Ni(0)	4-4	$\Delta R_{5in} = \sqrt{5R_1^2 + 10R_1\Delta R_{ } + 5\Delta R_{ }^2} - \sqrt{5}R_1$
Ni(0) - O(5c) - Ni(0)	4	$\Delta R_{5out} = \sqrt{5R_1^2 + 2R_1(4\Delta R_{11} + \Delta R_1) + 4\Delta R_{11}^2 + \Delta R_1^2} - \sqrt{5R_1}$
Ni(0) - O(5e) - Ni(0)	4	$\Delta R_{5_{011}} = \sqrt{5R_1^2 + 2R_1(\Delta R_1 + 4\Delta R_1) + \Delta R_1^2 + 4\Delta R_1^2} - \sqrt{5R_1}$
Ni(0)-Ni(6a)-Ni(0)	8	$\Delta R_6 = \sqrt{6R_1^2 + 2R_1(5\Delta R_1 + \Delta R_1) + 5\Delta R_1^2 + \Delta R_1^2} - \sqrt{6R_1}$
Ni(0)-Ni(6c)-Ni(0)	16	$\Delta R_6 = \sqrt{6R_1^2 + 4R_1(\Delta R_1 + 2\Delta R_1) + 2\Delta R_1^2 + 4\Delta R_1^2} - \sqrt{6R_1}$
Ni(0)-Ni(7a)-Ni(0)	4	$\Delta R_{\rm 7in} = 2\sqrt{2}\Delta R_{\rm H}$
Ni(0)-Ni(7b)-Ni(0)	4	$\Delta R_{\text{7out}} = 2\sqrt{2R_1^2 + 2R_1(\Delta R_{\parallel} + \Delta R_{\perp}) + \Delta R_{\parallel}^2 + \Delta R_{\perp}^2} - 2\sqrt{2}R_1$

^a The atomic labels are referred to Figure 1.

TABLE 4: As Table 3 for the MS Paths Involved in the EXAFS Data Analysis of the Films in the Case of Polarization [100]

paths	degeneration	path length variation
Ni(0)-O(1a)-O(-1a)-Ni(0) and Ni(0)-O(1a)-Ni(0)-O(-1a)-Ni(0)	2	$\Delta R = 2\Delta R_{ }$
Ni(0)-O(1a)-Ni(4a)-Ni(0) and Ni(0)-O(1a)-Ni(4a)-O(1a)-Ni(0)	4-2	$\Delta R = 2\Delta R_{ }$
Ni(0)-Ni(2a)-Ni(-2a)-Ni(0) and Ni(0)-Ni(2a)-Ni(0)-Ni(-2a)-Ni(0)	4-2	$\Delta R = 2\sqrt{2}\Delta R_{\rm H}$
Ni(0)-Ni(2b)-Ni(-2b)-Ni(0) and Ni(0)-Ni(2b)-Ni(0)-Ni(-2b)-Ni(0)	4-2	$\Delta R = 2\sqrt{2R_1^2 + 2R_1(\Delta R_{ } + \Delta R_{\perp}) + \Delta R_{ }^2 + \Delta R_{\perp}^2} - 2\sqrt{2}R_1$
Ni(0)-Ni(2a)-Ni(7a)-Ni(0) and Ni(0)-Ni(2a)-Ni(7a)-Ni(2a)-Ni(0)	8-4	$\Delta R = 2\sqrt{2}\Delta R_{\rm H}$
Ni(0)-Ni(2b)-Ni(7b)-Ni(0) and Ni(0)-Ni(2b)-Ni(7b)-Ni(2b)-Ni(0)	8-4	$\Delta R = 2\sqrt{2R_1^2 + 2R_1(\Delta R_{ } + \Delta R_{\perp}) + \Delta R_{ }^2 + \Delta R_{\perp}^2} - 2\sqrt{2}R_1$
Ni(0)-O(1a)-O(5a)-Ni(0)	8	$\Delta R = 1/2[(1+\sqrt{2}+\sqrt{5})\Delta R_{\parallel}]$
Ni(0)-O(1a)-O(5c)-Ni(0)	8	$\Delta R = \frac{1}{2} [\Delta R_{\rm II} + \sqrt{2R_{\rm I}^2 + 2R_{\rm I}(\Delta R_{\rm II} + \Delta R_{\perp}) + \Delta R_{\rm II}^2 + \Delta R_{\perp}^2} + \frac{1}{2} + $
$\mathbf{N}_{i}^{i}(0) = \mathbf{O}(1_{0}) = \mathbf{N}_{i}^{i}(2_{0}) = \mathbf{N}_{i}^{i}(0)$	0	$\sqrt{5R_1^2 + 2R_1(4\Delta R_{ } + \Delta R_{\perp}) + 4\Delta R_{ }^2 + \Delta R_{\perp}^2 - (\sqrt{2} + \sqrt{5})R_1]}$
NI(0) = O(1a) = NI(2a) = NI(0)	0	$\Delta R = 1/2(2 + \sqrt{2})\Delta R_{\parallel}$
Ni(0) - O(1a) - Ni(2b) - Ni(0)	8	$\Delta R = 1/2[\Delta R_{ } + \Delta R_{\perp} + \sqrt{2R_{1}^{2} + 2R_{1}(\Delta R_{ } + \Delta R_{\perp})} + \Delta R_{ }^{2} + \Delta R_{\perp}^{2} - \sqrt{2}R_{1}]$

Appendix

In section 2.3, we have discussed the number of scattering paths considered to simulate the theoretical EXAFS signal. Here, all of these paths are described in detail, for the [100] polarization, referring to Figure 1. Note that a negative shell number (e.g., Ni(-2a)) refers to the atom obtained from that reported in Figure 1 with positive shell number (e.g., Ni(2a)) by axis reflection. The scattering paths involved in the analysis of the reference sample were (i) all of the single scattering paths (SS) from the 1st to the 7th coordination shell; (ii) the collinear multiple scattering paths (MS) involving Ni(0)–O(1a)–Ni(4a)– O(1a)–Ni(0), Ni(0)–O(1a)–Ni(4a)–Ni(0), Ni(0)–Ni(2a)–Ni(0), Ni(0)–Ni(2a)–Ni(0), Ni(0)–Ni(2a)–Ni(0), Ni(0)–Ni(2a)–Ni(0), Ni(0)–Ni(2a)–Ni(0), ni(0)–Ni(2a)–Ni(0); and (iii) triangle path involving Ni(0)–O(1a)–O(5a)–Ni(0).

Regarding the film analysis, we have said that the introduction of the polarization removes the degeneration of several scattering paths. As an example, the SS contribution from the 1st coordination shell is split in two different contributions when a polarization along the [100] direction is taken into account: the first path has a component along the polarization direction and involves two first neighboring atoms (O(1a) and O(-1a), see Figure 1), whereas the second one has a null component along the polarization direction and involves four first neighboring atoms (O(1b), O(-1b), O(1c), and O(-1c)). The intensity of this last contribution is negligible with respect to the previous one. The same happens for the successive SS and MS paths, so that 29 different paths have to be considered in the data analysis, as reported in detail in the first column of Tables 3 and 4 for SS and MS paths, respectively. All of these 29 different paths are characterized by different interatomic distances. In Tables 3 and 4 (third columns), we report the analytical expressions for the variation in scattering path lengths, caused by pseudomorphism, defined as the difference between the scattering path lengths in the bulk and in the film cases respectively, in terms of variations of the in-plane (ΔR_{\parallel}) and out-of-plane (ΔR_{\perp}) Ni–O interatomic distances. All of these 29 paths have been weighted by the corresponding degeneration factors (second columns in Tables 3 and 4). Because of the symmetry of the system, the number and the type of the paths obtained in the case of polarization along the [001] direction are the same.

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