Common fingerprint of hydroxylated non-polar steps on MgO smoke and MgO films

L. Savio¹,a, M. Smerieri¹,a,b, A. Orzelli⁰,b, L. Vattuone¹,a,b, M. Rocca¹,a,b, F. Finocchić, J. Jupilleć

¹IMEM-CNR, Via Dodecaneso 33, 16146 Genova, Italy
òUniversità di Genova, Dipartimento di Fisica, Via Dodecaneso 33, 16146 Genova, Italy
ćInstitut des Nanosciences de Paris, UPMC Université Paris 06, CNRS UMR 7588, 140 rue de Lourmel, 75015 Paris, France

A R T I C L E  I N F O

Article history:
Received 25 September 2009
Accepted for publication 13 November 2009
Available online 29 November 2009

Keywords:
Magnesium oxide
Hydroxylation
Vibrational spectroscopy
Scanning tunneling microscopy
Density functional theory
MgO smoke
MgO film
Hydroxylation

A B S T R A C T

The infrared spectra of MgO smoke exposed to water are compared to high-resolution electron energy loss spectra (HREELS) of hydroxylated ultrathin MgO(1 0 0)/Ag(1 0 0) films. Very similar bands are observed at 3458–3480 cm⁻¹ and 3710–3714 cm⁻¹. On the basis of first principle calculations, these bands are interpreted as the stretching modes of the two distinct OH groups that are formed at monoatomic steps parallel to (1 0 0), crystallographic directions. The lower frequency band is due to H adsorbed on O at the step edge, while the higher frequency one originates from OH groups that are twofold coordinated with Mg. Consistently, scanning tunneling microscopy images of MgO films, prepared in similar conditions as during the HREELS experiments, show that the MgO/Ag(1 0 0) island edges are mainly nonpolar, i.e. oriented along the (1 0 0) direction. In spite of that, a minor contribution to the OH-stretch intensity from hydroxylated polar (1 1 0) steps cannot be excluded; for such geometry density functional theory predicts indeed a single OH species with a vibrational frequency very close to the high-frequency band of OH adsorbed at (1 0 0) steps.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Surfaces of crystalline oxide involve defects such as steps, kinks, adatoms and vacancies, which are similar to those described in the Kossel model of cubic ionic crystal surfaces [1]. On metals and semiconductors, the properties of surface defects are commonly studied by means of stepped surfaces of defined orientations that are obtained experimentally by appropriately cutting bulk crystals along high Miller index (HMI) planes [2]. However, the method often fails in the case of oxides. As observed on MgO [3] and on α-Al₂O₃ [4], the annealing at a temperature high enough to reorder HMI surfaces results in steps bunching in such manner that neither step orientation nor step height can be controlled. On the other hand, cleavage produces, aside mono-atomic steps, also an uncontrollable distribution of multi-atomic steps and slip lines [5].

An alternative approach to obtain well defined surface orientations consists in producing oxide crystallites of reproducible size distribution under accurately controlled conditions. For instance, it was shown by photoluminescence [6,7] and infrared (IR) spectroscopy [7,8] that MgO smoke, which mostly consists of cubic crystallites with (1 0 0) facets of average size 100–200 nm, involves a high density of defect-free (1 0 0) mono-atomic steps [6,7]. During the infrared experiments, water adsorption was performed under a partial pressure of 20 Pa of water vapour, i.e. in conditions close to the ambient. Both photoluminescence [6,7] and IR data [7,8] (the latter ones also supported by calculations) consistently define unambiguous fingerprints for (1 0 0) MgO steps on MgO(1 0 0) surfaces and demonstrate that MgO smoke can be used as a high area model to study the behavior of these sites. Supported MgO thin films are commonly used to model MgO(1 0 0) substrates in ultra-high vacuum (UHV) experiments [9–11]. We have deposited them on Ag(1 0 0) due to the small lattice mismatch between the two crystal structures, which allows the growth of ordered layers. On Ag(1 0 0), the adsorption of oxygen atoms atop Ag atoms is energetically favoured (a situation mirrored in the opposite case of Ag films grown on MgO(1 1 0) [12]), so that the oxygen lattice of the MgO(1 0 0)/Ag(1 0 0) film matches the silver lattice [13]. Consistently, a general agreement exists about the epitaxial relationship (1 0 0)MgO//(1 0 0)Ag with (1 0 0)MgO//(1 0 0)Ag [9–11]. Nevertheless, the orientation of edges and steps of the MgO islands is still debated. STM images collected by Schintke et al. [10] and Sterrer et al. [11] show MgO domains with edges running mostly parallel to the non-polar (1 0 0) directions. A very different behavior was reported by Valeri et al. [9], whose STM data show edges predominantly oriented along the (1 0 0) direction. Straight (1 1 0) steps are formed either by O or Mg atoms so that Mg and O rows alternate along the direction normal to the step edge in a polar sequence [14,15].

The purpose of the present paper is to compare steps on MgO smoke to steps on MgO(1 0 0)/Ag(1 0 0) films and to discuss their polar or non-polar nature on the basis of the vibrational signatures.

---

¹ Corresponding author. Tel.: +39 010 3536292; fax: +39 010 3622790. E-mail address: savio@fisica.unige.it (L. Savio).

0039-6028/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2009.11.013
detected upon H$_2$O dissociative adsorption. To this aim the vibrational spectra of MgO samples exposed to water vapour are discussed with the support of calculation performed within the density functional theory (DFT). Although the spectroscopic data and part of the numerical results have already been published [8,16], no specific analysis was performed in order to distinguish among the different orientations of the steps. Moreover, the interpretation of the high-resolution electron energy loss (HREELS) spectra of the OH/MgO films that was originally given in Ref. [16] is here revisited and strengthened through the comparison with the IR data collected on MgO smokes [8].

The hydration of MgO smokes has been analyzed at the Institut des Nanosciences de Paris. Infrared (IR) spectroscopy and DFT calculations evidenced the vibrational signatures of the fully hydroxylated non-polar (1 0 0) mono-atomic steps of MgO [6,8]. The structure and the hydroxylation of ultrathin MgO(1 0 0)/Ag(1 0 0) films have been studied at the Department of Physics of Genoa by scanning tunnelling microscopy (STM) and HREELS [16,17], respectively. Most interestingly, a close comparison of the two series of experiments shows that HREELS and IR spectra present similar features. That observation renews our interest in determining the actual orientation of the borders of the Ag-supported MgO films. To clarify this point we discuss here: (i) the structure of clean MgO/Ag(1 0 0) films prepared in conditions very similar to the ones examined by HREELS, as inferred by STM investigation; (ii) the comparison of experimental IR and HREELS data with DFT predictions about the vibrational spectra for hydroxylated polar and non-polar steps of MgO(1 0 0).

The critical assessment of the spectroscopic measurements that were performed on MgO films [16], crystalline surfaces studied in ultra-high vacuum, and on MgO smoke, high surface area samples exposed to pressure close to the ambient [8], makes it possible to appraise the basic properties of extended defects, such as steps, through surface systems that differ by preparation and dimensions. This also suggests that these very properties can be interpreted as the fingerprints of the defects, irrespectively of the host surface system.

2. Experimental and theoretical methods

Only the most important aspects of the setups dedicated to STM and vibrational analysis will be recalled here, since they were previously described in detail in Refs. [7,16,18]. The features distinguishing the data on MgO smokes from those previously collected by other authors are due to the experimental protocol. The MgO powder was synthesized and manipulated in a controlled environment, that is, either in a pure argon and oxygen mixture or under vacuum. Such precautions proved to be imperative to pinpoint the photoluminescence spectra of defect-free (1 0 0) steps [6] and the related IR spectra upon hydroxylation [8]. HREELS and STM experiments were performed in two different ultra-high vacuum (UHV) chambers equipped with the same instrumentation for film growth. The MgO/Ag(1 0 0) films were grown by reactive deposition at a substrate temperature T = 453 K and 500 K in the two chambers, respectively. This method, consisting in the Mg evaporation on Ag(1 0 0) in presence of an O$_2$ atmosphere, is commonly used [9,10] since it leads to films of better crystallographic quality than those obtained either by oxidation of a pre-deposited Mg film [19,20] or by sputter deposition [20]. In our experimental setup, the O$_2$ partial pressure was limited to P$_{O_2} = 3 \times 10^{-7}$ mbar since the gas is introduced in the UHV chamber through a doser placed at 2 cm from the Ag(1 0 0) surface; the local pressure at the sample is therefore 5 to 10 times higher. The Mg flux (\(\phi\)) was evaluated a priori through a quartz microbalance (\(\phi = 0.23 \pm 0.03\) ML/min, in monolayers of MgO) and checked a posteriori by analysis of the frequency and intensity of the Fuchs–Kliewer (FK) modes recorded by HREELS or of the STM images. Water vapour adsorption was then studied by HREELS (Detail 0.5 by Specs) in ultra-high vacuum conditions [16], while structural characterization was performed using a low temperature STM (Createc) operated with liquid N$_2$. The use of cryogenic temperatures allows the sample to remain uncontaminated for several days and therefore to probe accurately different sample areas. The lateral size of STM images and the orientation of the surface were determined from atomically resolved measurements of the clean Ag(1 0 0) surface (see inset of Fig. 4); similarly, heights were calibrated on mono-atomic Ag steps.

The calculations were performed within the generalized gradient approximation [21] to the Density Functional Theory. After a fine optimization for various structural models, the OH frequencies and intensities were computed within the density functional perturbation theory (DFPT) using the ABINIT code [22]. Here we use the default O and H norm-conserving pseudo-potentials [23], with an energy cutoff of 30 Hartree (816 eV). More details can be found in Refs. [8,24].

The stability of water on surfaces that differ by orientation or by the type of defects (O and MgO vacancies, mono- and diatomic steps) has been evaluated as a function of temperature T and water partial pressure P through the adsorption free energy \(\Delta G_{\text{ads}}(P,T)\). The latter quantity was approximated by the DFT adsorption energy, \(E_{\text{ads}}\), computed at \(T = 0\) K, plus the \((P,T)\)-dependent chemical potential of water vapour, as detailed in Ref. [25]. Therefore, for each adsorption configuration, we can sketch (Fig. 1) the coexistence curves, which correspond to \(\Delta G_{\text{ads}}(P,T) = 0\). Each curve splits the \((P,T)\) plane in two domains: above the coexistence curve, the actual adsorbed phase is predicted to be thermodynamically stable; below, the vapour phase is stable.

3. Results and discussion

For clarity sake, in the following O$_h$ and Mg$_b$ will indicate atoms of the MgO substrate, while O$_a$ will refer to an oxygen coming from a dissociated water molecule.

![Fig. 1. Computed stability diagram of water adsorption at different MgO adsorption sites. Each curve represents the \((P,T)\) values for which \(\Delta G_{\text{ads}}(P,T) = 0\), as a function of the surface configuration (see Section 2). Above (below) the curve, the adsorbed (vapour) phase is stable. The curves are plotted together for an easier comparison and correspond to the \((3 \times 2)\) water monolayer on MgO(0 0 1) (dark red +), to the hydroxylated diatomic step with edges parallel to [0 1 0] (magenta +), to the hydroxylated mono-atomic step with edges parallel to [0 1 0] (blue +) and to the hydroxylated MgO divacancy on MgO(0 0 1) (green +). The corresponding curve for the hydroxylated mono-atomic step on MgO(0 0 1) with edges parallel to [1 1 0] is out of scale. The error bars account for the error propagation, which is due to the estimated uncertainty in \(E_{\text{ads}}\) as computed within the GGA as well as to the dispersion of \(E_{\text{ads}}\) as a function of the density of adsorbed hydroxyls on the defects. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
3.1. IR spectra from smokes and HREEL spectra from supported films

Fig. 2 reports the IR and HREEL spectra in the $\nu_{OH}$ stretching region for the hydroxylated MgO smoke and ultrathin film, respectively. The corresponding vibrational frequencies calculated by DFPT are also reported for comparison. The IR spectrum recorded after hydration of MgO smoke (by exposure to water vapour at a pressure of 20 Pa) was shown in Fig. 1 of Ref. [8]. The HREEL spectrum was collected for a 2.8 ML thick MgO(1 1 0)/Ag(1 0 0) film after an exposure to 20 Langmuir H$_2$O at 310 K (see Fig. 2A of Ref. [16] – 1 Langmuir $= 1 \times 10^{-6}$ torr $\times$ s). The OH stretching frequencies are very similar for both samples: $\nu_A = 3480$ cm$^{-1}$ and $\nu_B = 3710$ cm$^{-1}$ on MgO smoke and $\nu_A = 3458$ cm$^{-1}$ and $\nu_B = 3714$ cm$^{-1}$ on the MgO film. At odds with the narrow $\nu_A$ and $\nu_B$ peaks that are present in HREEL and IR spectra, a broad structure at ~3600 cm$^{-1}$ is recorded for MgO smoke only. This suggests the occurrence of several H-bonded configurations, which might come from fully or partially dissociated water. Either partially wet (1 0 0) terraces surrounded by fully hydroxylated mono-atomic (1 0 0) steps or hydroxylated multi-atomic steps could explain this broad feature (see the corresponding calculated frequencies in Fig. 3).

We underline that the comparison between vibrational spectra and computed frequencies is based on the pre-requisite that the corresponding adsorption configurations are stable in the experimental conditions (see Fig. 1 and Section 2).

Fig. 3 summarises the results of DFT calculations of the OH stretch frequency for different OH–MgO configurations that could possibly fit the IR bands [8]. After an examination of both their frequencies and intensities, it is found that these bands can only be accounted for by the fully hydroxylated mono-atomic steps oriented along the (1 0 0) direction [8]. Indeed, adsorbed OH groups on low-index MgO(1 1 1) and MgO(1 0 0) surfaces are rejected on the basis of the comparison with experiment. Water dissociation on multi-atomic steps oriented along the (1 0 0) direction, as represented by diatomic steps, is discarded since neither adsorption at steps edges or in hollow sites, nor the full hydroxylisation could explain the ($\nu_A$, $\nu_B$) set and, in particular, the $\nu_A$ band at 3480 cm$^{-1}$. After considering various configurations associated with mono-atomic (1 0 0) steps – including isolated molecules, adsorption at kinks, saturation of both steps and terraces – the best fit was found for the fully hydroxylated step [8].

In particular, the full OH-covered (3 1 0) surface is discarded because the very intense peak expected at 3130 cm$^{-1}$ is not observed [8]. Finally, the agreement of the experimental IR intensity ratio $I_A/I_B = 2$ with the calculated value confirms that the (Os–H, Mg–OwH) decoration of the mono-atomic (1 0 0) steps of MgO is responsible for the two IR bands at $\nu_A = 3480$ cm$^{-1}$ and $\nu_B = 3710$ cm$^{-1}$. The similarity of the OH related frequencies observed for MgO smoke and films suggests that also in the latter case they can be associated with the fully hydroxylated mono-atomic (1 0 0) step. However, experiment [9] and theory [26,27] suggest that MgO(1 0 0)/Ag(1 0 0) domains with polar edges can be also present, stabilized by the surrounding silver islands in which they are embedded. This point is now discussed in light of a STM analysis of films similar to those previously investigated by HREELS and of DFT simulations.

3.2. STM analysis of MgO(1 0 0)/Ag(1 0 0) films

Fig. 4 shows a typical STM image of a clean MgO(1 0 0)/Ag(1 0 0) film, evaporated in similar conditions as those used during the HREELS analysis. The nominal thickness of the film (i.e. the average thickness as determined by “a priori” calibration through the quartz microbalance) is 1.5 ML but the local coverage of this particular portion of the sample is likely to be higher. The image shows the formation of MgO islands distributed on three different levels, separated by mono-atomic steps of height 2.3 ± 0.1 Å (see line scan in Fig. 4). The surface is entirely covered by MgO since: (a) MgO islands show a bias dependence with respect to the Ag substrate [27]; Such dependence is not observed in the present case, to indicate the homogeneity of the surface; (b) clean Ag(1 0 0) shows much larger terraces and steps oriented along the (1 1 0) direction. The observed profile is thus indicative of the formation of multilayer MgO islands.

We note that our images are qualitatively similar to those obtained by Schintke et al. (see Fig. 1 of Ref. [10]), who observed (1 0 0) mono-atomic MgO step edges on 0.3 ML as well as on 2.0 ML thick films. In fact, in spite of the slightly higher disorder of our film, the edges of the MgO islands are mainly parallel to the (1 0 0) directions of the Ag(1 0 0) substrate. As previously reminded, this means that the non-polar (1 0 0) orientation for the edges is preferred over the polar one. Therefore, the present STM investigation confirms, a posteriori, the dominance of hydroxylated (1 0 0) steps on the 2.8 ML thick MgO film previously analyzed by HREELS [16].

3.3. Vibrational signature of hydroxylated non-polar (1 0 0) and polar (1 1 0) steps of MgO(1 0 0)

Here we carry out a theoretical study of the hydroxylation of the polar (1 1 0) edge, in order to compare it to the OH-covered (1 0 0) edge. In the case of stoichiometric MgO domains, straight charged (1 1 0) edges generate a growing electrostatic potential along the normal direction [15], contrary to step edges parallel to (1 0 0) which are neutral. As a consequence, large MgO islands with (1 1 0) steps are generally much less stable than those having neutral borders [14], unless electrically compensated by the metallic substrate, by adsorption of charged species or by step reconstructions [26,27]. As done previously for (1 0 0) steps on MgO(1 0 0) [24], mono-atomic steps on MgO(1 0 0) surfaces are simulated herein through periodic slabs terminated by vicinal surfaces. The (5, 0, –1) geometry is employed as a model for non-polar steps (see Fig. 5b), while polar edges are reproduced with vicinal (8, 1, –1) and (14, 1, –1) surfaces (Fig. 5a). On the (8, 1, –1) slab,
the steps edges that follow each other are formed by alternating rows of Mg and O atoms; on the (14, 1, 0) slab, on the contrary, successive step edges are all formed by a given atomic species. The Mg-terminated rows at the top of the slab are compensated by O-terminated rows at the bottom of the slab.

We model dissociative water adsorption by decorating either Mg atoms with OH groups (Mg–OwH) or O atoms with protons.
of the polar groups whenever present. This raises the question of a contribution uniquely reactive towards water and are expected to be covered by OH smoke, the bands at 3480 and 3710 cm

smoke, the bands at 3480 and 3710 cm

smoke, the bands at 3480 and 3710 cm

smoke, the bands at 3480 and 3710 cm

smoke, the bands at 3480 and 3710 cm

smoke, the bands at 3480 and 3710 cm

because of charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.

For all these reasons the HREEL spectrum again supports the presence of a majority of OH-decorated monatomic (1 0 0) steps on the hydroxylated MgO(1 0 0)/Ag(1 0 0) film. The HREEL spectra are taken on 2.8 ML thick films, so that a large amount of OH decorating steps are in a configuration that is locally similar to pure MgO. In such a case, hydroxyls on polar (1 1 0) steps vibrate at a unique frequency, while the adsorption of OH on non-polar (1 0 0) steps gives rise to the (vA,vB) doublet previously discussed. This conclusion is not affected by charging effects and border deformations of the overlayer, which, if large enough, can possibly shift the frequency but can hardly change the very nature of the adsorbed hydroxyls. In the case of a MgO monolayer on Ag(1 0 0), a full simulation of the many possible OH adsorption geometries should be carried out, but this is out of the scope of the present paper.