

Molecular Adsorption on Thin Ordered Oxide Films and Single Crystal Oxide Surfaces

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Abstract. We report adsorption studies on clean and modified surfaces of NiO, Cr₂O₃ and Al₂O₃. Small molecules such as NO, CO and H₂O are adsorbed. The oxides are studied as bulk single crystals as well as as single crystal films. We are able to discriminate between adsorption on ideal terrace sites and defect sites by using EEL-spectra of surface states.

Employing various methods, e.g. ARUPS, HREELS and NEXAFS, we characterize the bonding between molecules and oxide substrates and show that concepts known from molecule metal interactions cannot directly be transferred to oxide surfaces.

1. Introduction

The electronic structure of metal surfaces is predominantly determined by the delocalized nature of the wavefunctions [1]. Localization of the electronic wavefunction in a metal, although present in certain cases, does not play the dominant role for a correct description of the electronic structure of a metal. Exceptions are, of course, the rare earths and actinides with their highly localized levels.

In oxides, on the other hand, localization is crucially important to even approximately understand the electronic structure. Often we are dealing with completely ionic or at least strongly ionic compounds, the constituents of which may be basically described as ions with their localized charges. Frequently, electron correlation plays a very important role to understand the electronic structure of the ions and to describe the transport properties of oxides. One case is NiO which is an example for a so called charge-transfer-insulator [2]. Compounds of this type have received a lot of attention in the past in particular with respect to photoemission and inverse photoemission [3].

The differences in electronic structure alluded to above between metals on one hand and oxides on the other hand are expected to have major consequences also for the interaction of the respective substrates with molecules from the gas phase, in the sense that concepts to describe molecule surface bonding developed

over the last two decades for metals cannot be simply transferred to try to understand bonding towards oxide surfaces.

Therefore several groups have started to investigate adsorption on oxide surfaces experimentally. We have chosen to use bulk oxide single crystal surfaces as well as thin epitaxial oxide films as substrates [4-7]. The main reasons to study both types of substrates are:

- i) Bulk single crystals may be cleaved in vacuo and stable surfaces with very few defects are created.
- ii) Thin oxide films with various crystallographic orientations including non-polar and polar surfaces may be grown on metallic substrates.
- iii) Through variation of the preparation conditions of the films the number and type of defects on such films can be varied and thus their influence on the adsorption behaviour may be studied in comparison to bulk single crystals.
- iv) Thin films on metal substrates can be cooled to liquid nitrogen or liquid helium temperatures without sacrificing the conductivity of the samples needed for application of electron spectroscopies.

Oxide surfaces play important roles in catalysis. Some transition metal oxides are catalytically active and others, mainly simple metal oxides are often used as support materials for catalysts. So far we have studied NiO(100) [8-14], NiO(111) [15-17], Cr₂O₃(111) [18-22], CoO(111) [23] and γ -Al₂O₃(111) [13,24-27]. Ni and Co ions prefer the oxidation state II+ and do not have the tendency to change oxidation states while Cr with oxidation state III+ in Cr₂O₃ may relatively easily change its oxidation state either to lower or higher values. In this sense NiO and CoO represent limiting cases as opposed to Cr₂O₃. Al₂O₃ is an example for a support oxide material.

2. Results and Discussion

2.1 NiO

The most thoroughly studied oxide surface in our laboratories is the non-polar surface of NiO, i.e. NiO(100), which we investigated both as a bulk single crystal surface and as a thin film.

We start our discussion by considering this surface. We shall, when possible, compare the properties of the NiO(100) surface with the polar NiO(111) surface. Figure 1 shows the ideal geometric arrangement for both surfaces. LEED investigations on the bulk NiO(100) surface reveal that the surface is rumpled by less than 0.02 Å with an inward relaxation of the surface layer by 0.04 Å which is about 2% [28]. In other words, the deviation from the bulk terminated structure is not dramatic. The quality of a cleaved NiO(100) surface, as indicated by the LEED pattern in Fig. 1, is quite comparable to the quality of metal single crystal surfaces, indicating that the number of point and line defects is rather low. While also NiO(100) [8,9] and NiO(111) [16,17] films exhibit distinct LEED patterns, the spot sizes are considerably larger and the background intensities are higher as

compared with the bulk single crystal indicating a higher density of defects on the film surfaces. The comparison of the bulk single crystal and film systems thus allows us to study the influence of defects on the adsorption properties [10,11].

Let us first consider the ideal clean (100) oxide surface. The electronic properties of the clean surface document themselves, among other things, in the existence of surface states [12]. These surface states are localized in the surface layer. For metal surfaces we know that their energy position and intensity, for example, in a photoelectron spectrum strongly depends on the presence of adsorbates on the surface. In the case of an oxide surface we have recently detected such surface states, however, not via photoemission but rather via electron energy loss spectroscopy [12]. Figure 2 shows the EEL-spectra of the electronic excitations of a bulk single crystal surface [29] and of a thin film. In comparison with the clean surfaces we show two spectra after adsorption of water and additional adsorption of NO. Several conclusions can be drawn from the observations: Water adsorption leads to the appearance of OH losses at 460 meV. Coupling to the substrate Fuchs-Kliewer phonons causes the side bands at higher loss energies to appear. The electronic excitations between 0.57 eV and 2 eV are, however, not influenced by water adsorption. On the other hand NO adsorption which shows up by the NO vibrational loss does affect these electronic excitations. In particular, the

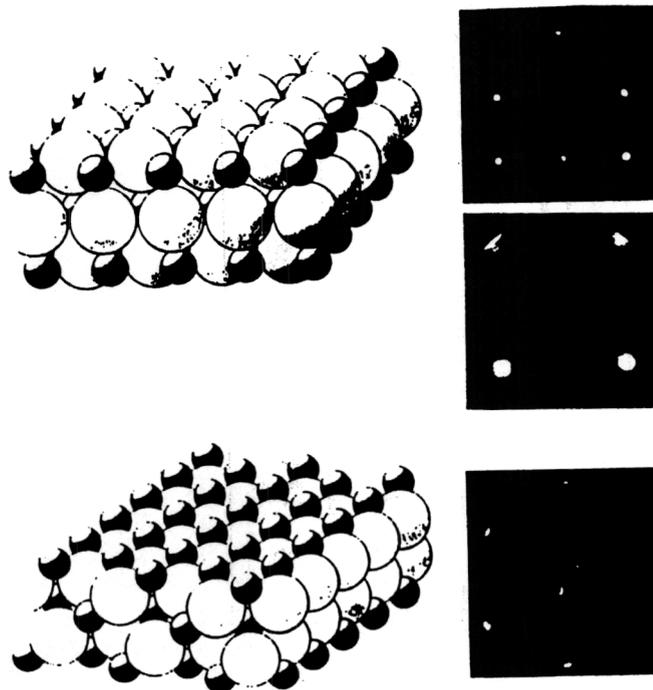


Fig. 1: Left panel: structural model for NiO(100) (top) and NiO(111) (bottom). Right panel: LEED patterns of single crystal NiO(100), NiO(100)/Ni(100), and NiO(111)/Ni(111).

bands at 0.57 eV and 1.62 eV of the clean surface are shifted to 0.9 eV and 1.75 eV, respectively.

These findings represent clear experimental evidence for the existence of surface states at oxide surfaces. The nature of these states has been explained through ab-initio cluster calculations [12]: The states between 0.57 eV and 2 eV are due to $d \rightarrow d$ transitions localized on the Ni ions. The lowest lying $d \rightarrow d$ transitions in bulk NiO occur at 1.05 eV and 1.79 eV and are due to excitations between the ground ${}^3A_{2g}$ -state and the ${}^3T_{2g}$ and ${}^3T_{1g}$ -states, respectively. They may be well described via electronic excitation within an octahedral NiO_6^{10-} cluster. The surface states can be derived from these bulk states by realizing that the Ni ions in the surface are coordinated only by five O^{2-} ions which reduces the ligand field strength with respect to the bulk and stabilizes the excited states. A particularly pronounced effect is observed for the lowest lying state shifting by 0.48 eV. It is this state that is strongly influenced by the presence of NO but not by OH. We believe that this is due to the preferential adsorption of OH on the defects at the surface while NO adsorbs preferentially on the regular NiO(100) terrace sites. As a consequence of the localization of the $d \rightarrow d$ excitations to the Ni^{2+} centers, the shift of the surface state proves that NO binds to the Ni^{2+} centers and not to the oxygen ions in the surface. This conclusion is in line with vibrational HREELS results where the stretching frequency is found close to the gas phase value which is compatible with this bonding configuration [8,9]. The NO axis turns out to be tilted by about 45° with respect to the NiO(100) surface

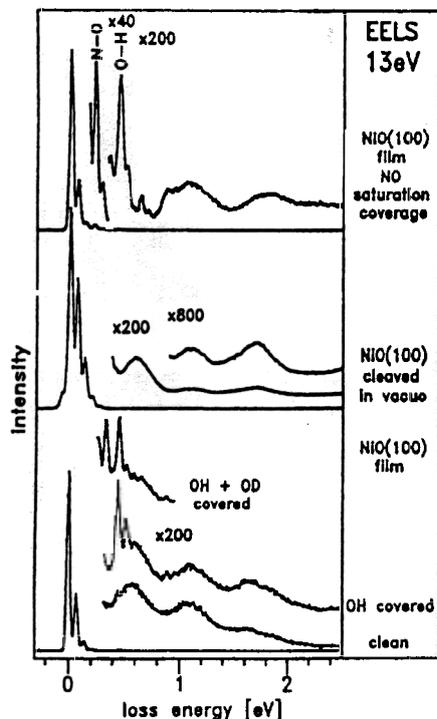


Fig. 2: ELS spectra in specular reflection at $E_p = 13$ eV of a) a cleaved NiO(100) surface, b) a clean thin NiO(100) film, c) a thin NiO(100) film after H_2O adsorption and d) a thin NiO(100) film after NO + H_2O adsorption.

normal as revealed through a NEXAFS analysis [8,9]. Together with the TPD data [8,9] which are compatible with an adsorption energy of 0.5 eV for both desorption from bulk and thin film NiO(100) surface the picture for the NO/NiO(100) system is rather complete. The experimental data on this system are complemented with theoretical analysis from several groups [30,31] which give a quite satisfactory rationale both for the binding energy as well as for the adsorption geometry. This will be discussed in another paper in this volume [32].

The nature of the OH bond to the NiO(100) surface is considerably less clear as compared with the NO-NiO(100) bond. Firstly, we can conclusively show that the loss at 460 meV is due to OH groups by using isotopic exchange experiments. A spectrum, where part of the OH groups is exchanged by OD groups is included in Fig. 2 [16]. Secondly, it was already mentioned that the hydroxyl groups do not seem to adsorb on regular terrace sites but rather on defects. Experiments with water adsorption on bulk single crystals with very low point defect density (very low background intensity in LEED) show that dissociative sticking of water with hydroxyl formation is widely suppressed, corroborating the idea that defects are involved in the process. If a weakly sputtered bulk single crystal is exposed to water, surface hydroxyls are formed. In the case of a NiO(100) surface OH can be removed through thermal treatment. A surface not saturated with hydroxyl groups exhibits a modified behaviour with respect to exposure towards other adsorbates, e.g. NO. Hydroxyl groups sometimes also influence the geometric structure of the surface and its thermal stability. The NiO(111) surface represents such a case [16]. We have indications that NiO(111), formed via oxidation of a Ni(111) surface and heated above the hydroxyl desorption temperature starts to facet. NiO(100) facets are formed on the surface. It is therefore difficult to completely remove the surface hydroxyls from the NiO(111) surface and study the completely clean surface.

With respect to a structural characterization NiO(111) is considerably more complicated as compared with NiO(100). The main reason is the ambiguity about surface termination, which may be either Ni or O termination in the case of NiO(111). Ion scattering spectroscopic (ISS) measurements indicate that the surface exhibits a mixed termination. Predosage of oxygen onto the NiO(111) surface strongly attenuates NO adsorption which led us to the conclusion that adsorption takes place preferentially on the Ni terminated patches. The NO adsorption behaviour on this surface is quite similar to the NiO(100) surface. NO does not have exactly the same but rather similar spectroscopic properties when adsorbed on NiO(100) and NiO(111). Bonding of NO towards NiO(111) appears to be slightly stronger, i.e. by about 10%, as revealed through TPD. We find desorption energies of 0.52 eV for NiO(100) and 0.59 eV for NiO(111). The adsorption behaviour of the NiO(111) surface, however, is considerably different from the NiO(100) surface. Several new NO adsorption states are observed on NiO(111) in TPD spectra when OH is removed from the surface. Most of the states exhibit desorption energies not very different from the ideal terrace site except for one state which has a desorption temperature of 450 K. This state may be due to the formation of a NO_2^- species through reaction of NO with O^- on the surface. We

do have experimental evidences from XPS data that such species may be present on the NiO surfaces of thin films [17]. This example illustrates how the presence of hydroxyl groups may influence the reactivity of an oxide surface. Bonding of CO on the NiO surfaces is considerably weaker than that of NO. Desorption temperatures are around 100 K. The experimental studies for CO adsorption have not yet been completed for NiO.

2.2 Cr₂O₃

Cr₂O₃(111) may be prepared by oxidation of Cr(110) [19,20]. Similar to NiO there are surface states on the Cr₂O₃(111) surface [19,20]. The surface is hexagonal and polar. Therefore the termination ambiguity discussed above for NiO(111) exists here as well. Electronic EEL-spectra show that the surface Cr ions adopt an oxidation state of 2+ as opposed to 3+ in the bulk. This means, the surface has a high reduction potential which is documented by the formation of oxygen adsorbates and simultaneous attenuation of the surface Cr²⁺ state. CO forms an ordered ($\sqrt{3} \times \sqrt{3}$)R30° structure on the Cr₂O₃(111) surface. The orientation of the molecular axis is peculiar in this case: The CO axis is oriented parallel to the surface plane as revealed by angle resolved photoemission and NEXAFS [18,20]. It is evident from the discussion presented elsewhere [18-20] that the bonding of CO to Cr₂O₃(111) is different from the bonding of CO to all metallic surfaces investigated so far.

2.3 Al₂O₃

As an example for a non-transition metal oxide we have investigated Al₂O₃. Aluminiumoxide is the prototype of a support material and particularly interesting in this respect. An Al₂O₃ layer with a quasi-hexagonal oxygen layer as the terminating surface may be grown via oxidation on top of a NiAl(110) alloy surface. The oxide layer is very thin, i.e. it exhibits a thickness of about 5 Å as revealed by XPS and AES. The structure of this film has been studied with various techniques including scanning tunnelling microscopy, LEED, EELS and ARUPS [24].

LEED indicates a well ordered structure with a large unit cell in real space. ISS measurements show that the oxide surface is oxygen terminated. The analysis of the intensity distribution among the LEED spots points to a hexagonal or quasi-hexagonal arrangement of oxygen atoms in the terminating layer.

This conclusion is corroborated by ARUPS measurements of the oxide band-structure dispersion parallel to the surface [4-7]. The experimental dispersion curves are shown in Fig. 3 together with a computer simulation for a distorted hexagonal oxygen 2p band structure. The oxygen-oxygen distance in the quasi-hexagonal oxygen layer is by about 6% larger as compared with bulk Al₂O₃ but this is compatible with the limited thickness of the film. The dispersions have

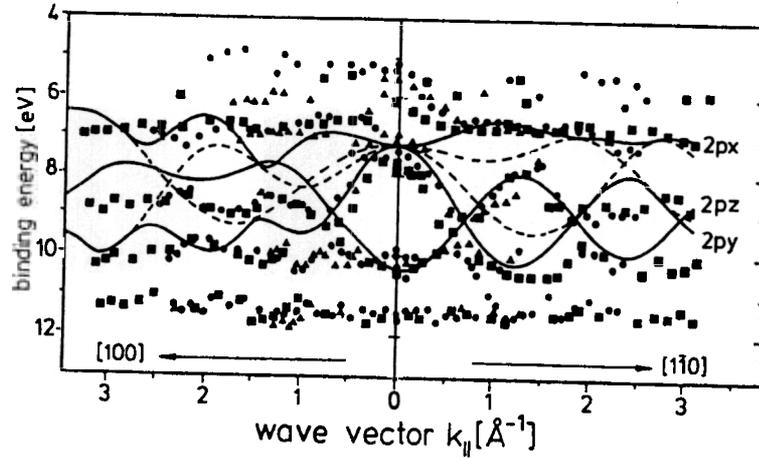


Fig. 3: Measured $k_{||}$ dispersion of a γ - $\text{Al}_2\text{O}_3(111)$ surface. The result of a tight binding band structure calculation of a two dimensional O^{2-} overlayer is compared with the experimental data.

been measured with respect to the two azimuths (110, 100) of the NiAl substrate and these are not high symmetry directions with respect to the oxide Brillouin zone. The calculations, which are described in detail elsewhere, reproduce the basic features of the bandstructure except for the two bands at the top and the bottom of the oxide band. These we assign to aluminium derived contributions indicating the aluminium-oxygen hybridization. What are the aluminium sites in the oxide? We believe from our HREELS data that this oxide film is related to a γ - $\text{Al}_2\text{O}_3(111)$ surface, i.e. there are octahedral and tetrahedral sites.

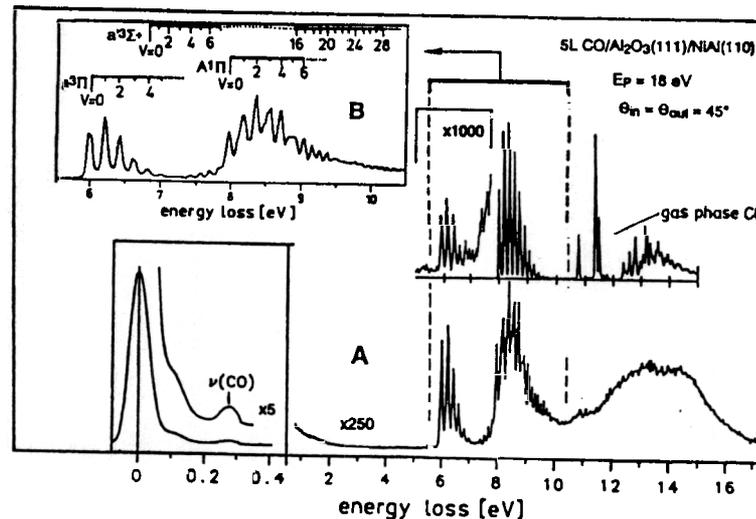


Fig. 4: EEL spectrum ($E_p = 18$ eV, $\theta_{in} = \theta_{out} = 45^\circ$) of 5 L CO on $\text{Al}_2\text{O}_3/\text{NiAl}(110)$ at $T = 35$ K in comparison with details of the CO gas phase spectrum ($E_p = 48$ eV).

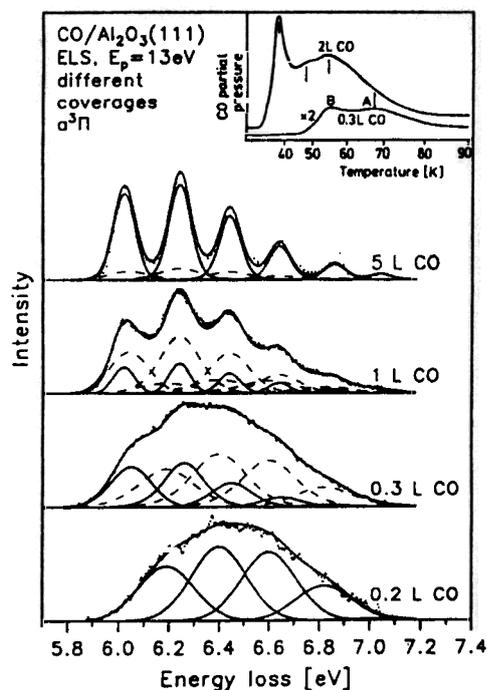


Fig. 5: EEL spectra of the $a^3\pi$ state of CO on Al₂O₃/NiAl(110) for different coverages. To the experimental data we have fitted vibrational progressions. The inset shows TPD spectra.

Most molecules interact with the γ -Al₂O₃(111) surface rather weakly. As an example we show in Fig. 4 ELS spectra of CO physisorbed on Al₂O₃ taken at 35 K [25]. The ELS spectra of the multilayer system show rather pronounced vibrational splitting of the electronically excited states. The comparison with gas phase spectra indicates the rather close correspondence. It is interesting to note that in the monolayer regime the line widths of the vibrational components increase and the bands shift to higher excitation energy which is demonstrated in Fig. 5 for the $a^3\pi$ excitation of CO. There are various CO states identifiable via their line positions and line widths in ELS and their TDS spectra (see inset in Fig. 5). On the basis of such results we can estimate the pressure one would have to apply in order to create a coverage similar to the low temperature situation at higher temperature [4-7].

2.4 Metal Deposits on Oxide Surfaces

One goal of our activities is to model a catalytic system by depositing metal on oxide surfaces. In the following we shortly refer to two examples for metal/metal-oxide systems:

Na/Cr₂O₃

Because alkali-metal promoters of metal oxide catalysts are well documented [33,34], it was near at hand to study alkali-metal deposition on Cr₂O₃(111) and the interaction of such composite systems with molecules from the gas phase. Since the catalytic activity of metal oxides is intimately related to the charge state of the surface atoms [8,9,18-20], a knowledge of the electronic structure at the surface is fundamental to understand the catalytic activity of these systems.

Most oxide systems exhibit very intense Fuchs-Kliewer phonon bands which can be quenched by overlayers which are in a metallic state [21]. Using HREELS and ARUPS we have studied the charge state of Na on Cr₂O₃ for H₂O and CO₂ adsorbates. The changes observed in the vibrational and the geometric structure of the oxide and the Na film are characteristic for a change of the charge state of the Na atoms from metallic to ionic upon either H₂O or CO₂ adsorption. For details we refer to ref. [21].

Pt/Al₂O₃

Pt/Al₂O₃(111) represents a model system for a catalyst where metals are deposited on a support material. Pt is evaporated from a source in situ and ultrathin Pt films are created at different surface temperatures. The structure of the Pt films and their interaction with the oxide surface is not completely understood yet but SPA-LEED and TDS of the CO covered films already show some characteristic features. The TDS data reveal in addition to a desorption signal between 350 K < T < 500 K, which is likely due to desorption from metallic Pt, a low temperature signal. The latter desorption peak we attribute to desorption from Al₂O₃ which is possibly modified by Pt atoms incorporated into the oxide material [7]. This interpretation is corroborated by SPA-LEED data which reveal that deposition of Pt partly destroys the order within the oxide film [35].

3. Synopsis

Summarizing we have characterized the electronic properties of oxide surfaces including transition metal oxides and simple metal oxides. It is shown that the metal cations in the surface are characterized by a specific ELS spectrum indicating the existence of particular surface states which are very important to understand the adsorptive behaviour of these surfaces. The surface states allow us to differentiate ideal terrace sites from defect sites on oxide surfaces. We have discussed the difference between polar and non-polar surfaces considering the stabilization induced by adsorption at defects. Physisorption and chemisorption of small molecules at oxide surfaces lead to interesting adsorption geometries. The bonding involved is very different on oxide surfaces as compared to metal

surfaces and the adsorption properties of the oxide surface are dramatically modified by depositing metal onto the surface.

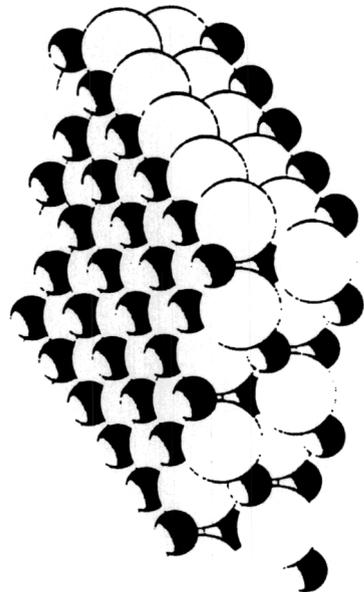
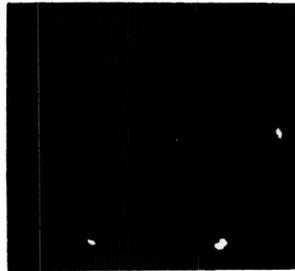
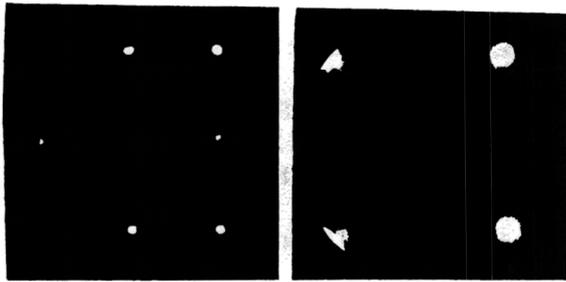
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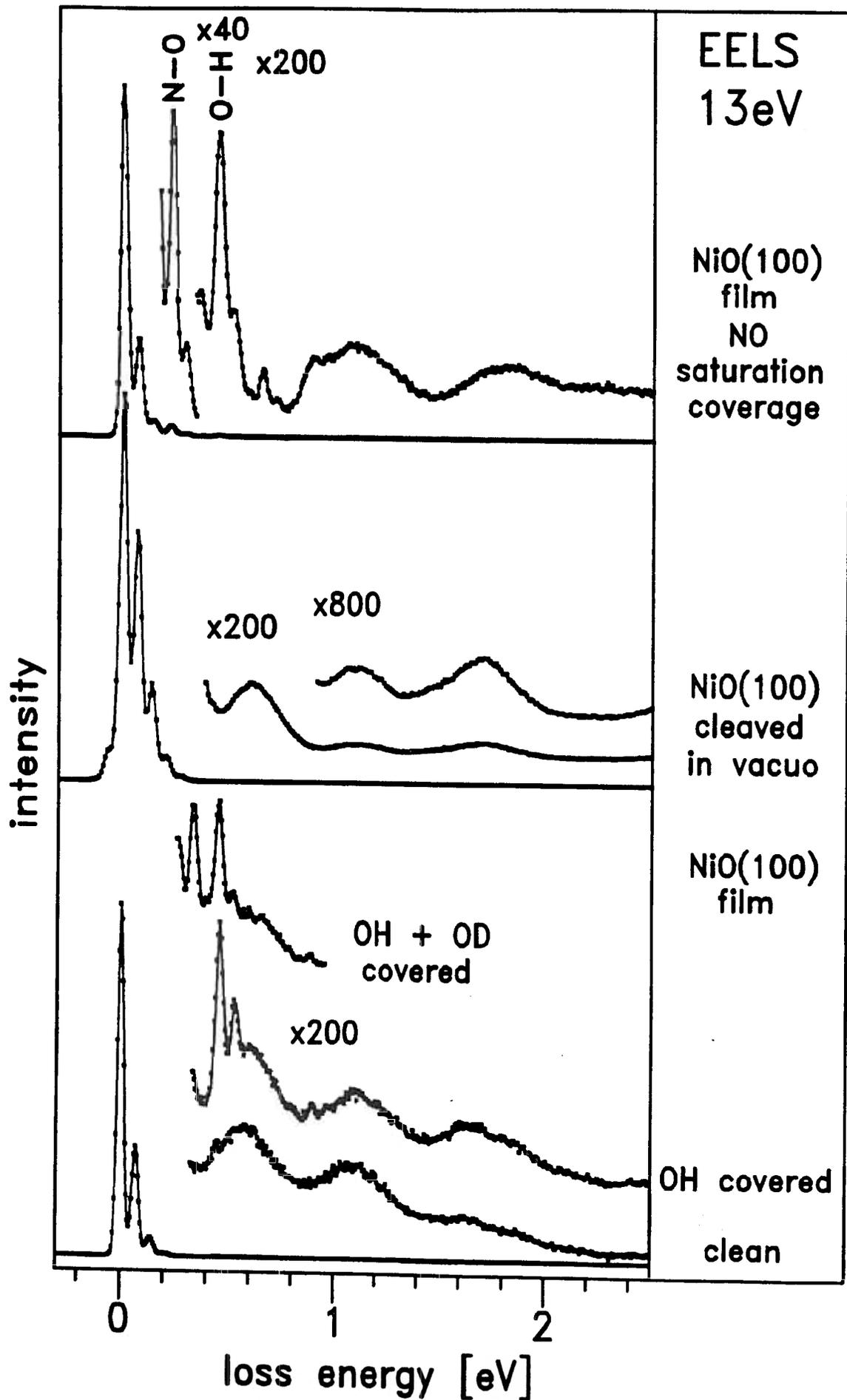
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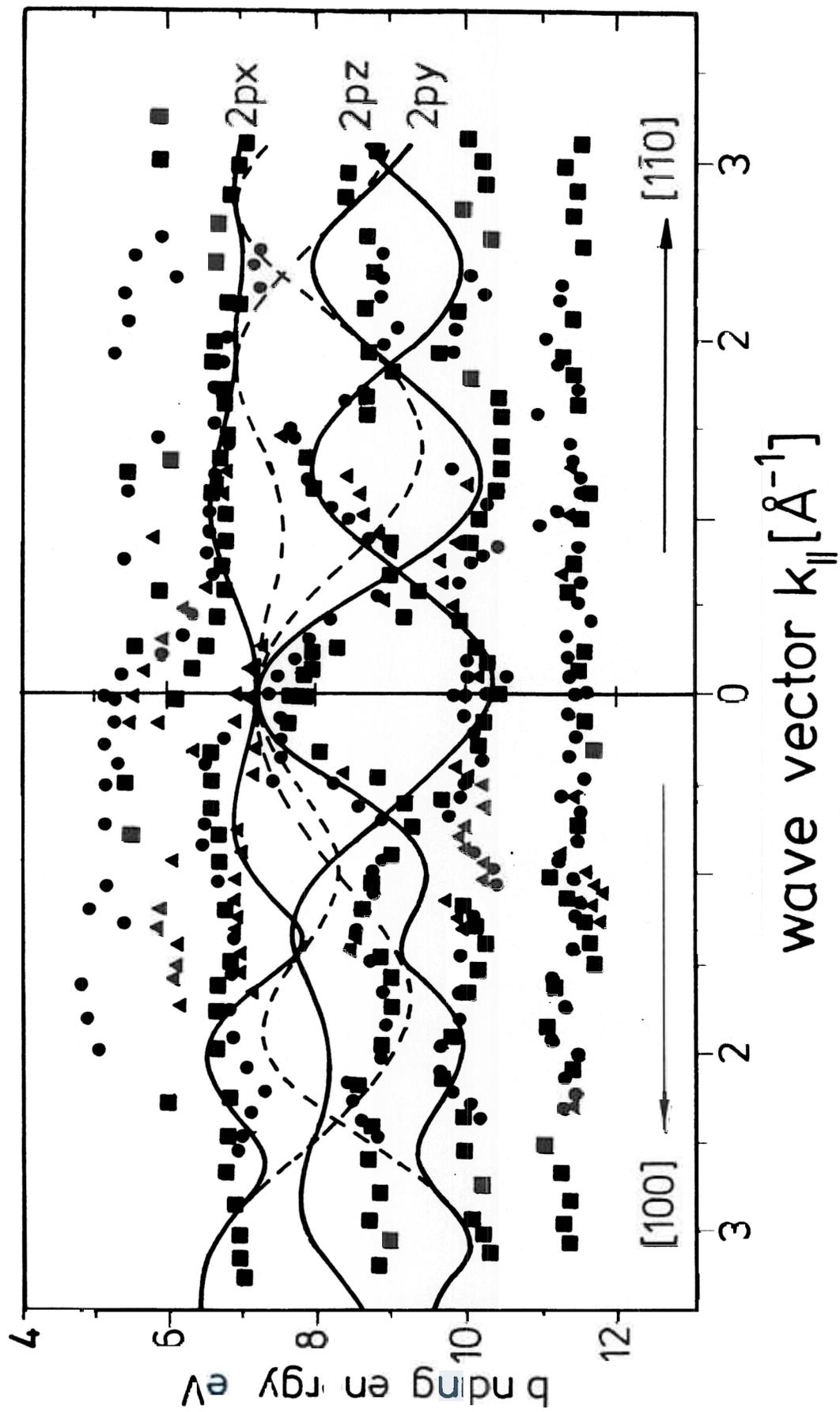


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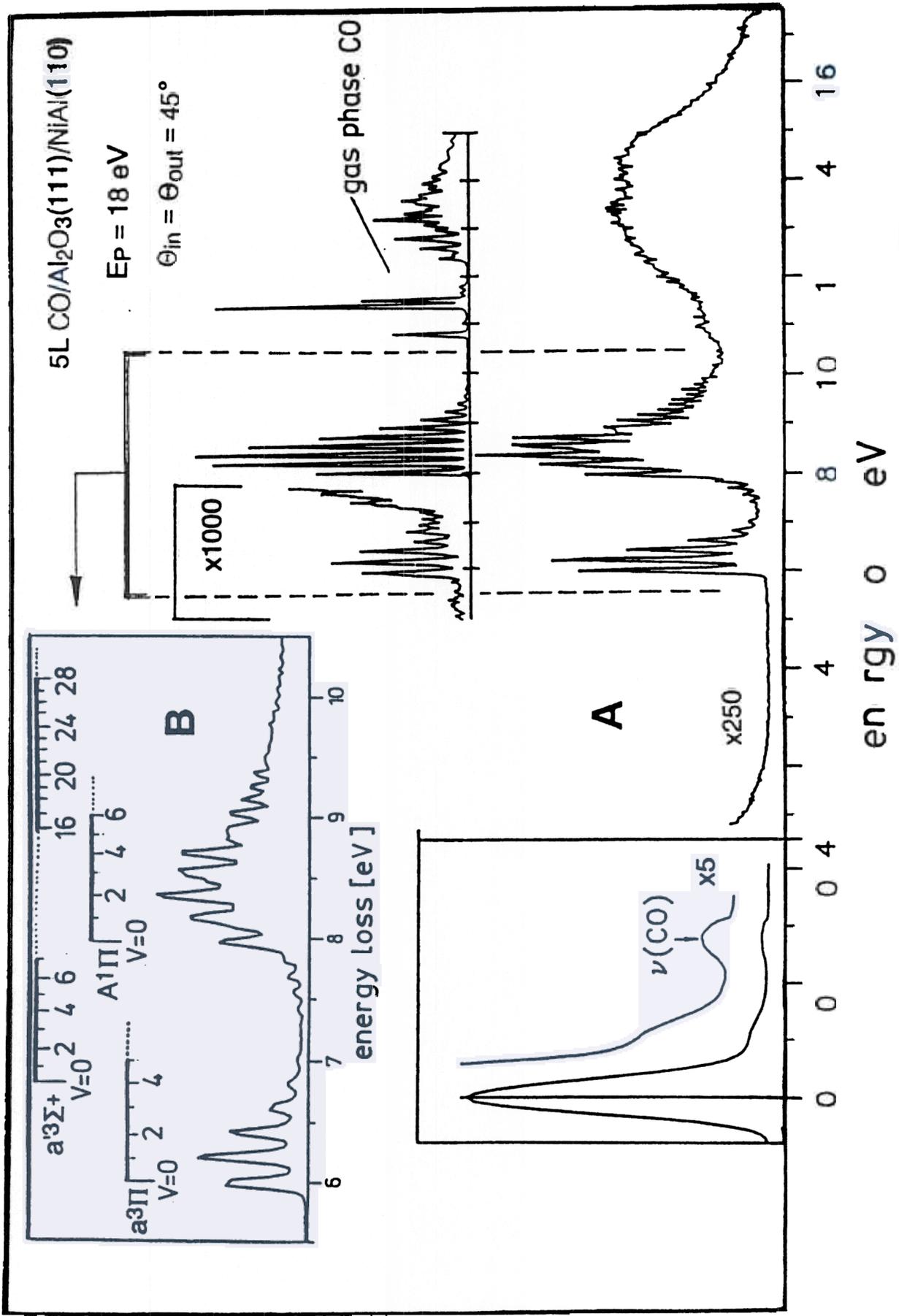


Fig 4

