# **Electronic Excitations at Oxide Surfaces**

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The present paper summarizes the possibilities to use electron energy loss spectroscopy (EELS) to investigate the electronic properties of systems with highly localized electronic states, such as oxide surfaces. Surface excitations may be clearly distinguished from bulk excitations in EELS, and eventually a ligand field spectroscopy may be developed on this basis. This ligand field spectroscopy is used to study surface phase transitions at oxide surfaces. Adsorbates influence the surface properties of oxides dramatically. Examples are discussed.

### 1. Introduction

It is well known from the investigation of metal surfaces, that within the gaps of the projected bulk band structure surface states exist which may be detected via photoemission if they are occupied or via inverse photoemission if they are unoccupied [1,2]. It is characteristic of such surface states that their energy exhibits no wave vector dependence with respect to a direction perpendicular to the surface plane. Also, surface states may be quenched or energetically shift upon interaction with adsorbates. The reason for the appearance of surface states, of course, is the change of the electronic structure at the surface with respect to the bulk. The atoms in the surface feel a different potential because their coordination number is reduced and consequently the energy levels change. Very recently, Bertel and coworkers [3] have developed a very appealing picture of how these surface states on metals influence the chemistry, i.e. adsorption at metal surfaces including aspects of coadsorption in the sense of poisoning and promoting effects. For oxide surfaces, photoemission has, so far, not been sucessfully applied to detect intrinsic surface states [5]. Neither in valence photoelectron spectroscopy nor in coreelectron spectroscopy has a clear detection of surface states on oxide surfaces been possible so far. This is somewhat surprising, but it is probably connected with the presence of strong many particle effects which are caused by localization phenomena in oxides, documented by intense satellite structure in the photoelectron spectra [4].

We shall discuss in the following how electron energy loss spectroscopy (EELS) can be used to clearly differentiate between surface and bulk excitations [6]. The examples are grouped in two parts. In the first part we shall discuss transition metal oxides with rock salt structure, namely NiO and related materials. In the second part we include corrundum type structures, such as  $Cr_2O_3$ , where the surface provides enhanced structural flexibility, in our discussion.

#### 2. Experimental Aspects

The experiments are performed in ultrahigh vacuum chambers which are equipped with preparation sections. Several techniques are being used to prepare the oxide surfaces [6]. Oxide surfaces may be prepared by cleavage of bulk samples or via the creation of epitaxially grown thin oxide films on top of metallic substrates. While with the former preparation method non-polar surfaces with equivalent number of cations and anions in the surface are often well accessible, polar surfaces of highly ionic surfaces cannot be easily prepared via cleavage. The latter type of surfaces may be prepared via epitaxial growth. In addition, via the control of the match or mismatch of film and substrate lattice constants the defect density of the oxide film may be controlled. The geometrical structure of the films may be characterized by electron diffraction (LEED) and by scanning tunnelling microscopy (STM). We employ electron spectroscopic methods such as UPS, XPS, AES, and particularly EELS and HREELS for the present study. We also use photon based methods such as IRAS and laser induced desorption [7].

#### 3. Results and Discussion

The idea is to excite electronic transitions of a transition metal ion which are optically forbidden for the free ion. These transitions are characterized by relatively small line widths, and they are energetically often located within the optical band gap of the material. Several groups have used EELS to identify such transitions for various materials [8-15]. A comprehensive collection of spectra accompanied by the appropriate interpretation can be found in the book by P.A. Cox [16]. Briefly, the situation relevant for the interpretation of the data is shown in Fig.1. A NiO(100) surface has been chosen as the example and shows the coordination of metal and oxygen ions in this case. We differentiate between the coordination in the second and deeper bulk layers of the rock salt structure and the one in the surface plane. Schematically the 3d orbital energies of the transition metal ion in the two surroundings are given in Fig.1. The depicted situation is representative for a single transition metal ion, but it is valid to a good approximation because the d-levels, especially of the late transition metals, are highly localized in space and the direct metal-metal coupling is negligible. Let us consider the bulk situation first: An octahedral field splits the d-orbitals in a threefold  $t_{2g}$ - and a twofold degenerate  $e_g$ set. Ni<sup>2+</sup> carries eight electrons, six occupying the t<sub>2g</sub>-set and two unpaired electrons the eg-set [17]. If the spin couplings are properly taken into account, this leads to a  ${}^{3}A_{2g}$  ground state. The two lowest lying excited states in this octahedral field are of  ${}^{3}T_{2g}$  and  ${}^{3}T_{1g}$  type and are situated at 1eV and 1.81eV respectively. If we reduce the ligand field by taking one of the ligands off, the symmetry as well as the repulsion is reduced [8]. This leads to splitting of the  $t_{2g}$  sub set into an e- and a  $b_2$ component, and of the  $e_g$  sub set into a  $a_1$ - and a  $b_1$ -component. At the same time the splitting in the d-levels is reduced and the excited states shift to lower energy, and their number increases. The calculated excitation energies for both coordinations in NiO are plotted as an energy level diagram in Fig.2. This figure also contains the calculated excitation energies for Co ions in CoO which is isostructural to NiO. Co in CoO, however, is in a  $d^7$  configuration. The excited



Fig. 1 Schematic representation of coordination at NiO(100) and in the bulk. Orbital energy diagrams are included.



Fig. 2 Total energy diagrams of the lowest d-d excitations in NiO and CoO at the surface and in the bulk.



Fig. 3 Comparison of the optical absorption spectrum of bulk NiO as compared with the EELS spectrum of a NiO(100) surface.

states are, of course, comparable to NiO, but there is one very low lying state in the case of the surface coordination [18], because the ground state of a  $d^7$  system in O<sub>h</sub> symmetry is a spatially degenerate  ${}^4T_{1g}$  state. The important point for the interpretation of the experimental data is to recognize that this spatial degeneracy of the ground state is lifted upon lowering the O<sub>h</sub> symmetry of the bulk coordination. This is the case for a Co<sup>2+</sup> ion within the ligand field of C<sub>4v</sub> symmetry on the CoO(100) surface. The splitting resulting from this effect is very small, i.e. the E state lies only 55 meV above the non-degenerate A ground state. The other excited states occur on the CoO surface at excitation energies slightly smaller as compared to NiO(100). The reason for this similarity is that the manifolds of states in a d<sup>7</sup> and a d<sup>8</sup> configuration are identical, but their energetic order is inverted. The bulk excitation is situated around 0.9eV and may be assigned on the basis of literature data. The surface excitation lies at 0.45eV, i.e. it is shifted to lower excitation energy with respect to the bulk.

Fig.3 contains the relevant experimental information for NiO [8,19]. The optical spectrum of the bulk sample is compared with an EELS spectrum of the NiO(100) surface. The band gap is marked by an arrow. Within the band gap the d-d excitations are localized. By aligning the peaks in the spectra several peaks may be identified as bulk transitions, except the lowest excited state which is only visible in the EELS spectrum [9,13,19,20]. We have shown that this peak clearly is due to the excitation at the surface because it shifts when molecules such as NO and CO are adsorbed onto the NiO(100) surface [8]. The surface excitations at higher excitation energies are covered by bulk excitations. Those have been studied also via spin polarized ELS measurements [11]. Fig.4 collects HREELS data for CoO(100) [18] in comparison with NiO(100) within the range of the very intense Fuchs-Kliewer phonon excitations. The predicted feature due to excitation of the E state at 55 meV



Fig. 4 EELS spectra of CoO in the range of the Fuchs-Kliewer phonon excitations in comparison with NiO.

is found in both the loss as well as the gain part of the HREELS spectrum. On the surface prepared by cleavage of a bulk sample the relative intensity of the peak close to the intense phonon peak is very small. The reason is the large sample volume, i.e. many oxide layers, contributing to the phonon intensity, while the surface state is only due to excitation in the first layer. If we, however, limit the thickness of the oxide by preparation of a thin, well structured oxide film we can decrease the relative intensity of the Fuchs-Kliewer phonons with respect to the surface excitation. This effect is seen in the second experimental trace shown in comparison with the cleaved bulk sample. Upon exposure of the surface to CO, for example, the surface state is quenched as indicated in the third trace from the bottom [18]. For comparative purposes we show in the topmost spectrum the corresponding range of Fuchs-Kliewer excitations in a NiO(100) thin film of comparable thickness. It is quite obvious that the low lying surface excitations are not present on a NiO(100) surface as predicted by the calculations [18].

Very similar studies have been undertaken for polar rock salt surfaces. NiO(111), CoO(111), and FeO(111) have been investigated [7,21-25]. These surfaces when prepared via oxidation of the corresponding metal single crystals are covered with a layer of hydroxyl groups, which stabilizes the polar surface by reduction of charge in the first layer. Upon removal of the hydroxyl layer the polar surface is destabilized and it restructures via the so called octopolar reconstruction. In this latter situation, microfacets of (100) orientation are formed on the surface. In these microfacets the vast majority of transition metal ions are in similar local environments as on the NiO(100) surface. EELS allows us to spectroscopically follow the changes in coordination upon reconstruction [21].

The above discussed structural rearrangement in NiO(111) involves several layers of the oxide. The mass transport involved leads to a relatively disordered surface indicated by diffuse LEED superstructure spots. There are other polar oxide surfaces, however, where the creation of the most stable surface does not involve



Fig. 5 LEED pattern of Cr<sub>2</sub>O<sub>3</sub>(0001) as a function of surface temperature a) 100K, b) 150K, c) 300K

more than the top layer. The (0001) surface of  $Cr_2O_3$  crystallizing according to the corrundum type has been recently studied in our laboratory in some detail [26-32]. The structural quality of a film prepared via oxidation of a Cr(110) surface is rather high as revealed by X-ray diffraction data [33]. LEED data [30,32] of a surface at low temperature (100K) exhibit the typical hexagonal pattern of  $Cr_2O_3(0001)$  surface (see Fig.5). As the temperature of the surface is changed the LEED pattern of the surface changes. Fig.5a-c shows the sequence of LEED patterns observed. At 150K a  $(\sqrt{3}x\sqrt{3})30^{\circ}$  superstructure is observed, which becomes diffuse as the temperature reaches room temperature [30,32]. We can follow this transition by investigating the intensity of the first order superstructure spot as a function of temperature. This is shown in Fig.6a. It appears that there are two phase transitions involved in the transformation, namely an order-to-order transition from low to intermediate temperature, and a order-to-disorder transition from intermediate to room temperature. In order to see this more clearly, we look at the I/V curves of the superstructure spot in Fig.6b. Two temperatures are compared. At 150K where the spot is very sharp and at 300K where its intensity is rather diffuse. Obviously, the I/V behaviour is very similar except that the amplitude of the maximum is strongly decreased. This is another strong indication that the surface sites involved in the low temperature and in the high temperature transition are identical. The comparison of the temperature dependence of the main structure spot intensity (I/V-curve in Fig. 6c) with the superstructure spot intensity in Fig.6a corroborates this conclusion. It is near at hand to speculate that the observed phase transitions are connected with the positions of the Cr ions in the surface layer. ELS spectra can now be used to identify the sites involved in the process [30]. Fig.7 shows EELS spectra taken from the clean, flashed oxide surface at two temperatures together with the results of the calculations. At 90K the



Fig. 6 LEED intensities for  $Cr_2O_3(0001)$ 

a) as a function of temperature

b) I/V-curves of the superstructure spot for two surface temperatures

c) I/V-curve of the main structure spot for 100K.

spectrum exhibits two signals at loss energies of 1.2 eV and 1.4 eV, denoted by A and B respectively. They are accompanied by a broad feature C at about 1.8eV. As the temperature rises to 300K, signals A and B loose relative intensity whereas the relative intensity of feature C increases. In order to proove the surface nature of the features we studied the influence of adsorbates onto the spectral features (not shown here). The spectra in the considered energy range change dramatically indicating that all three features are due to surface excitations see below). The surface feature C also overlaps with some bulk excitations as revealed by comparison with information from bulk chromia samples [34] and ruby crystals [35]. The central idea for the interpretation of the data is that the various surface excitations are connected with Cr ions in different sites at the surface. The population of the sites changes as a function of temperature, and this gives rise for the temperature dependent changes in the EELS spectra, and concommitantly causes the observed phase transitions. Quantum chemical ab-initio cluster calculations by V. Staemmler and his group [30] may be used to corroborate these ideas. The clusters used consist of one  $Cr^{3+}$  ion surrounded by either six  $O^{2-}$  ions which form a slightly distorted octahedron (bulk  $Cr_2O_3$ ) or by three  $O^{2-}$  ions which represent the next neighbours of



Fig. 7 EELS spectra of  $Cr_2O_3(0001)$  at two different temperatures in comparison with calculations of d-d excitation energies for various surface sites of  $Cr^{3+}$ , the bulk site and a free  $Cr^{3+}$  ion.

a  $Cr^{3+}$  ion at the  $Cr_2O_3(0001)$  surface. This cluster is embedded in an quasi infinite or quasi semiinfinite field of point charges +3e and -2e which simulate the Madelung field of the chromiumoxide ionic crystal, assumed to have the bulk geometric structure.  $Cr^{3+}$  is a d<sup>3</sup> system and its electronic state in the gas phase is a <sup>4</sup>F state. This <sup>4</sup>F state is split within a regular octahedral field into a  ${}^{4}A_{2g}$  ground state, a first excited  ${}^{4}T_{2g}$  and a second excited  $T_{1g}$  state. The threefold degenerate states are further split by 0.02eV by the slight distortion of the octrahedral symmetry in Cr<sub>2</sub>O<sub>3</sub>. The lowest excitation energies are calculated at the CASSCF level to be 1.73 eV ( ${}^{4}T_{2g}$ ) and 2.73 eV ( ${}^{4}T_{1g}$ ). At the oxide surface the Cr<sup>3+</sup> ions are exposed to a weaker field due to the removal of half of the oxygen coordination sphere. The symmetry is reduced to below  $C_{3v}$  symmetry. Therefore one may expect on the basis of the experience with the rock salt oxides that the energy differences between the components of <sup>4</sup>F are smaller at the surface than in the bulk, and that quasidegeneracies of the  $T_{2g}$  and the  $T_{1g}$  levels are split further. The next step in our analysis is to consider the structure at the Cr<sub>2</sub>O<sub>3</sub> surface. Fig. 8 shows schematic drawings of the surface in the stable chromium terminated configuration, i.e. with half the Cr ions removed. There are three possible sites for the metal ions to reside on the surface, denoted by 1,2, and 3. These three sites correspond to three different ligand fields at the surface, and consequently to three different surface excitation spectra. Fig. 7 compares the calculated excitation energies with the experimental spectra at lowest and at highest temperatures. The clusters used for the calculations are schematically represented. For energetic reasons site 2 is unfavourable. The



Fig. 8 Schematic representation of a  $Cr_2O_3(0001)$  surface.

above qualitative arguments are confirmed by the calculations: For all three positions both the  ${}^{4}T_{2g}$  and the  ${}^{4}T_{1g}$  states are lowered considerably with respect to the  ${}^{4}A_{2g}$  ground state and are slightly split ( ${}^{4}T_{2g}$  into  ${}^{4}A_{1}$  and  ${}^{4}E$ , and  ${}^{4}T_{1g}$  into  ${}^{4}A_{2}$  and  ${}^{4}E$ ). Despite of these similarities, the d-d spectra of the Cr<sup>3+</sup> ions at the three nonequivalent sites differ to some extent. Due to the weaker ligand fields, the  $Cr^{3+}$ ions at sites 2 and 3 have considerably different excitation energies from those at site 1. The interpretation of the EELS spectra on the basis of the CASSCF calculations is rather straightforward. The high energy part of the broad signal C between 1.7 eV and 2.2 eV contains the  ${}^{4}T_{2g}$  state of bulk  $Cr_{2}O_{3}$  and the  ${}^{4}E$  surface component of the  ${}^{4}T_{1g}$  state of  $Cr^{3+}$  in site 1. The low energy part of signal C which is to a large extent quenched upon adsorption is attributed mainly to the surface component of the  ${}^{4}T_{1g}$  state of the same ions and probably also to the  ${}^{2}E$  bulk state which is not included in the calculations. Finally, the signals A and B are probably the surface excitations correlating with the first excited  ${}^{4}T_{2g}$  state of bulk Cr<sub>2</sub>O<sub>3</sub>. It is the split into the  ${}^{4}A_{1}$  and  ${}^{4}E$  component that gives rise to the observed doublet. As a function of temperature, the EELS intensity moves from the positions A and B towards C concommitant with the increasing population of site 3 with increasing temperature. This temperature dependent occupation of sites allow us to explain the observed phase transitions: At low temperature the Cr ions all occupy site 1 on the surface. At 150K the appearence of a  $(\sqrt{3}x\sqrt{3})R30^\circ$  superstructure indicates the formation of a larger unit cell. This could be accompanied by the correlated motion of half of the Cr ions from site 1 into site 3. A driving force for such a rearrangement could be the magnetic coupling between the Cr ions in the first and the second transition metal ion layers as discussed elsewhere. At higher temperatures the two different  $Cr^{3+}$  sites are statistically occupied, giving rise to a unit mesh typical for a lattice gas. This again leads to a p(1x1) structure with very diffuse intensity in the range of the superstructure positions.



Fig. 9 Infrared-absorption -reflection spectra of  ${}^{16}O_2$  and  ${}^{18}O_2$  adsorbed at two surface temperatures.

Interestingly enough, the above described phase transitions may be strongly influenced by the presence of adsorbates. There are adsorbates that quench the phase transition, like for example molecular oxygen, but there are also adsorbates that seem to stabilize the phase transition at 150K. An example is CO [27]. We know that CO lies flat on the surface. Our assumption is that it interacts with two  $Cr^{3+}$  ions on the surface which, of course have to have the right interatomic separation to allow for optimal bonding. The idea is that only when Cr ions are in neighbouring sites 1 and 3 simultaneously, the CO molecule can be stabilized on the surface thus stabilizing the phase transition. In order to investigate how molecular oxygen on the other hand destabilizes the phase transition [28] we have performed IRAS experiments [30,36] employing a combined HREELS/IRAS apparatus described in detail elsewhere [37]. Fig.9 shows a series of FTIR spectra recorded after the  $Cr_2O_3$  surface has been dosed with oxygen at 80K until saturation is reached, and heated in steps to 300K afterwards. Three features are observed.

We find absorptions between 963 cm<sup>-1</sup> and 984 cm<sup>-1</sup>, as well as at 1011cm<sup>-1</sup>, and at 1024 cm<sup>-1</sup>, due to adsorbed oxygen. As has been discussed before [28,36] the absorptions are due to the existence of distorted molecular oxygen at lower temperatures and atomically bound oxygen at higher temperatures. The atomically bound oxygen forms double bonds towards the Cr ions which are identified by comparison with IR spectra of chromyl species [38] that exhibit vibrational frequencies very close to those observed in the present data. There is even the splitting in the chromyl absorptions visible in the spectra. This is due to the inphase and out-of phase combinations of two chromium-oxygen double bonds in a geminal configuration. Most importantly the resolution of the IRAS experiments is high enough to allow for isotopic labelling experiments. Some data are included in Fig.9. They are fully consistent with the existence of molecular oxygen at low temperature and atomic oxygen at high temperature. At high temperature, in the range of atomic oxygen on the surface we realize that although we have dosed the surface only with <sup>18</sup>O<sub>2</sub>, the formed chromyl bonds involve <sup>18</sup>O as well as <sup>16</sup>O, indicating that exchange with the lattice oxygen occurs. The temperature sequence also shows that this starts at rather low temperature. Returning at this point to the quenching of the phase transition by adsorption of molecular oxygen, it is quite clear how, via the formation of the chromyl species that the mobility of the chromium ions is blocked so as not to allow for the necessary site hopping to undergo the phase transition.

#### 4. Conclusions

We have shown that the electronic structure at oxide surface may be studied via electron energy loss studies in the regime of low lying electronic excitations. A ligand field spectroscopy may be established that allows us to differentiate between sites of different coordination in the surface. Applying this spectrocopy it is possible to follow the rearrangements within surface phase transitions occuring at rather low temperatures on the  $Cr_2O_3$  corrundum (0001) surface. Adsorbates may be employed to support the surface nature of the above discussed excitations by using the so called "crud test", but they may also be used to either stabilize or destabilize surface phase transitions. It is shown that IR absorption spectrocopy may be successfully applied to the study of thin film oxides, opening up the field of more catalytically oriented studies. For  $Cr_2O_3$  surface states associated with charge-transfer excitations are identified.

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