

## Electronic surface states of NiO(100)

A. Freitag, V. Staemmler

*Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, W-4630 Bochum, Germany*

D. Cappus, C.A. Ventrice Jr., K. Al Shamery, H. Kühlenbeck and H.-J. Freund

*Lehrstuhl für Physikalische Chemie 1, Ruhr-Universität Bochum, Universitätsstrasse 150, W-4630 Bochum, Germany*

Received 1 February 1993; in final form 27 May 1993

The electronic structure of the (100) surface of NiO has been studied using EELS (electron energy loss spectroscopy) and ab initio calculations. In addition to the previously documented bulk excitations of NiO, two new states at energies of 0.57 and 1.62 eV have been found. These states are attributed to d-d transitions of the nickel surface ions. As expected for surface states, they are affected by the interaction with an adsorbate, i.e. adsorption of NO leads to a shift to higher energy. Ab initio cluster calculations show that the electronic structure of the surface is considerably different from that of the bulk which is a result of the lower symmetry of the crystal field at the surface ( $O_h \rightarrow C_{4v}$ ). The nature of the observed surface states has been identified by a comparison of the experimental data with theoretical results.

Due to the importance of oxides in catalysis the investigation of the properties of NiO has a long history in surface science. Despite the apparent interest in NiO only in the last few years a certain degree of agreement about the bulk electronic structure of NiO and related transition metal oxides could be established [1-6]. In this Letter, we deal with the electronic properties of the (100) surface of NiO. Since it is the surface region which interacts with adsorbates, a fundamental understanding of its electronic properties is of considerable importance for the understanding of catalytic processes at surfaces. From our analysis, we have found two distinct surface states for NiO(100). The only other documented oxide surface which shows a surface state is the  $Cr_2O_3$ (111) surface [7,8], but this state is due to the reduced ionic charge of the surface ions which is not the case for NiO(100).

The NiO(100) films have been prepared by oxidation of a Ni(100) single crystal surface. Cycles of oxidation at elevated temperature in an oxygen atmosphere followed by annealing were repeated until the LEED (low energy electron diffraction) pattern indicated the formation of an ordered oxide film. The

details of this procedure and the apparatus used have been described elsewhere [6].

A comparison between an EELS (electron energy loss spectroscopy) spectrum of the clean NiO(100) surface with spectra of the OH contaminated and the NO-covered surfaces is shown in fig. 1. At energies below 500 meV, the losses due to the NiO phonons and the NO and OH vibrational modes are visible as narrow features. In the spectra of the clean and the hydroxylated surface, four electronic transitions are observed at energies of 0.57, 1.1, 1.62, and 1.87 eV. Except for the existence of vibrational losses due to the hydroxyl groups in the spectrum of the OH contaminated surface, these two spectra do not differ very much. However, when the surface is dosed with NO, the spectrum changes considerably. At 235 meV the N-O stretching vibration becomes visible, and the loss at approximately 670 meV we have tentatively assigned to a combination of NO and OH vibrations. The electronic excitation at 0.57 eV is missing now, and a shoulder at 0.9 eV in the peak at 1.1 eV is found instead. Additionally, the two peaks at 1.62 and 1.87 eV now form one broad loss at 1.78 eV. The sensitivity of the losses at 0.57 and 1.62 eV towards adsorption indicates that they are due to

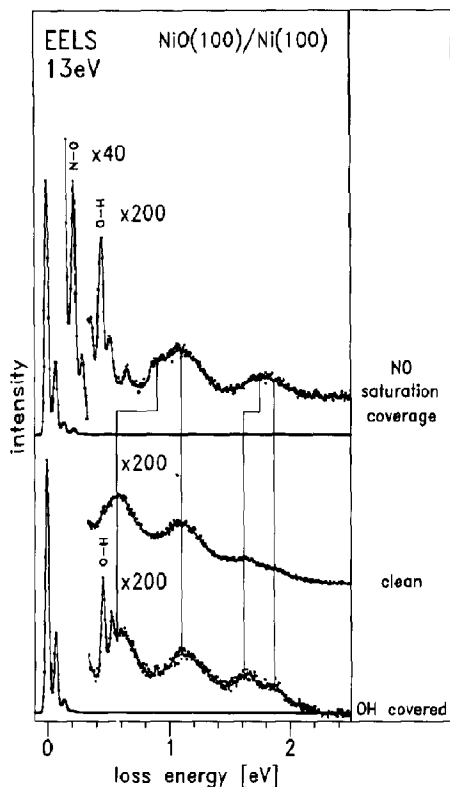


Fig. 1. Electronic excitation spectra of the clean, the hydroxylated, and the NO-covered NiO(100) surface ( $E_p = 13$  eV). Since the defects on the NiO(100) surface interact strongly with water, in the spectrum of the NO adsorbate also signals due to OH are observed.

surface states. The interaction of NO with the oxide surface shifts the peak at 0.57 to 0.9 eV and the loss at 1.62 eV is shifted in such a way that together with the loss at 1.87 eV it forms the broad peak at 1.78 eV. Therefore, we conclude that only two losses due to electronic excitations in the bulk are contained in the spectra, i.e. the losses at 1.1 and 1.87 eV, whereas the losses at 0.57 eV (0.9 eV with an NO adsorbate) and 1.62 eV ( $\approx 1.75$  eV) are due to surface states. These conclusions are in full agreement with results of the ab initio calculations presented below.

Interestingly, the surface states are only sensitive towards NO adsorption whereas it does not matter whether OH groups are present or not. As will be shown in a different publication [9], the hydroxyl species adsorbs at the defect sites of the NiO films, whereas NO occupies regular surface sites. There-

fore, we are led to the conclusion that the surface states are located at regular NiO surface sites.

An EELS spectrum similar to that of the clean surface shown in fig. 1 was obtained formerly by Cox and Williams [10]. However, they did not observe the surface state at 0.57 eV, which is most likely due to an insufficient energy resolution. Apart from this, their spectrum is quite similar to our spectrum. Since they did not perform adsorption experiments, they attributed the loss at 1.62 eV (1.66 eV according to their data) to a bulk transition of NiO.

Gorschlüter and Merz [11] recently also studied the electronic excitations of NiO(100) with EELS. They also observed the loss at 0.57 eV which they tentatively assigned to a surface state of NiO but the second surface state at 1.62 eV was not found.

For the quantum chemical ab initio calculations of the electronic states of bulk NiO and the NiO(100) surface, we have chosen a cluster consisting of one  $\text{Ni}^{2+}$  ion and six (for bulk NiO) or five (for a  $\text{Ni}^{2+}$  surface ion) neighbouring  $\text{O}^{2-}$  ions embedded in an infinite (bulk) or semi-infinite (surface) Madelung field of point charges ( $\pm 2 e_0$ ). The octahedral symmetry and the bulk Ni-O distance of 2.08 Å [12] were fixed throughout the calculations. Since the low-lying excited states of bulk NiO, below the optical band gap at about 4.0 eV, are local d-d excitations of the  $\text{Ni}^{2+}$  ions [3], our rather small clusters are sufficient for a reliable prediction of the lowest excitation energies. The  $\text{NiO}_5^{8-}$  cluster can as well be used to describe a  $\text{Ni}^{2+}$  ion next to a  $\text{O}^{2-}$  vacancy (infinite Madelung field) as a surface  $\text{Ni}^{2+}$  ion (semi-infinite Madelung field). In both cases the  $\text{O}_h$  symmetry of NiO is reduced to  $\text{C}_{4v}$ .

Our ab initio calculations have been performed as follows. First, a restricted open-shell SCF calculation has been carried out for the ground state of the cluster ( ${}^3A_{2g}$  for bulk NiO,  ${}^3B_1$  for  $\text{Ni}^{2+}$  at the surface).  $\text{Ni}^{2+}$  has a  $3d^8$  ground state configuration with  $t_{2g}^6 e_g^2$  occupation. The SCF orbitals were then used for a valence CI calculation in which either only the 3d-AOs of  $\text{Ni}^{2+}$  (VCI(d)) or the 3d-AOs and all 2p-AOs of the  $\text{O}^{2-}$  ions (VCI(dp)) were included. In the former case we had to localize the valence orbitals [13] in order to separate the 3d-AOs from the 2p-AOs. Alternatively, we also performed CASSCF calculations with the 3d-AOs in the active space; however, the results were very close to those of



Table 1

Calculated d-d excitation energies of bulk Ni<sup>2+</sup> in comparison with experimental data. FOCl and OA mean first-order CI and optical absorption spectroscopy, respectively. All energies are given in eV

	Occupation		NiO <sub>6</sub> <sup>10-</sup>				Exp.			
	t <sub>2g</sub>	e <sub>g</sub>	VCI		MC-CEPA	FOCI ref. [3]	OA		EELS	
			(d)	(dp)			ref. [21]	ref. [22]	ref. [10]	this work
<sup>3</sup> A <sub>2g</sub>	6	2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<sup>3</sup> T <sub>2g</sub>	5	3	1.00	0.86	1.00	1.04	1.13	1.08	1.05	1.10
<sup>3</sup> T <sub>1g</sub>	4	4 <sup>a)</sup>	1.72	1.50	1.81	1.77	1.95	1.86	1.79	1.87

<sup>a)</sup> Strong mixture with the second <sup>3</sup>T<sub>1g</sub> state with t<sub>2g</sub><sup>5</sup>e<sub>g</sub><sup>3</sup> occupation.

Table 2

Calculated d-d excitation energies of Ni<sup>2+</sup> at the NiO(100) surface, near to an O<sup>2-</sup> vacancy, and with an NO molecule bound to a surface Ni<sup>2+</sup> ion. The NO molecule was coordinated to the Ni<sup>2+</sup> ion of the cluster at a distance of 2.38 Å. The bond angle was 45°. For comparison also experimental excitation energies are given for the NiO(100) surface states. All energies are in eV

	NiO <sub>5</sub> <sup>9-</sup> , surface			NiO <sub>5</sub> <sup>9-</sup> , vacancy			ON-NiO <sub>5</sub> <sup>9-</sup> VCI		Exp., surface	
	VCI		MC-CEPA	VCI		MC-CEPA	(d)	(dp)	clean	NO-covered
	(d)	(dp)		(d)	(dp)					
<sup>3</sup> B <sub>1</sub>	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
<sup>3</sup> E	0.65	0.54	0.62	0.56	0.42	0.47	0.75	0.63	0.57	0.90
<sup>3</sup> B <sub>2</sub>	1.00	0.86	0.98	1.09	0.93	1.08	1.00	0.86		
<sup>3</sup> A <sub>2</sub>	1.30	1.11	1.21	1.22	1.00	1.03	1.42	1.22		
<sup>3</sup> E	1.44	1.22	1.38	1.47	1.21	1.40	1.52	1.31	1.62	≈ 1.75

between them (<sup>3</sup>A<sub>2</sub>, <sup>3</sup>E) is small. This behaviour can also be traced back to the different stabilization of the 3d-AOs in the reduced ligand field of C<sub>4v</sub> symmetry, but the explanation is more complicated since <sup>3</sup>T<sub>1g</sub> is a mixture of the configurations t<sub>2g</sub><sup>4</sup>e<sub>g</sub><sup>4</sup> and t<sub>2g</sub><sup>5</sup>e<sub>g</sub><sup>3</sup> [25].

A NO molecule bound to the NiO(100) surface at the Ni<sup>2+</sup> site will – at least partly – fill the vacancy of the missing O<sup>2-</sup> ion and strengthen the ligand field in the z direction. Therefore, the lowest <sup>3</sup>E state will be shifted to higher energies. Our calculations have been performed for a Ni<sup>2+</sup>-N distance of 2.38 Å (NO tilted by 45° and with the N end towards the surface [6]) and gave a shift of ≈ 0.2 eV both for the lowest <sup>3</sup>E state and the lowest <sup>3</sup>A<sub>2</sub> and <sup>3</sup>E components of <sup>3</sup>T<sub>1g</sub>. It should be noted that for tilted NO the degeneracy of the <sup>3</sup>E state is lifted and that each triplet state gives rise to a doublet state and a quartet state because of the interaction of the unpaired electron of NO with the Ni<sup>2+</sup> states. Since these splittings are

only of the order of 0.01–0.03 eV they are not documented here.

In tables 1 and 2 the results of the calculations for the low-lying triplet states are compared with experimental data. The assignment of the bulk excitations is in agreement with that of the other authors (see table 1). A comparison of the energies of the experimentally observed surface states with the theoretical results shows clearly that the loss at 0.57 eV (0.9 eV with an NO adsorbate) must be assigned to the <sup>3</sup>E state. For the other surface state at 1.62 eV (≈ 1.75 eV) the assignment is less clear. It may be assigned to the <sup>3</sup>A<sub>2</sub> or to the <sup>3</sup>E surface state, or to a superposition of both.

As may be seen from tables 1 and 2, the results of the MC-CEPA calculations reproduce our experimental data for bulk NiO and the clean NiO(100) surface within about 0.1 eV. Only for the surface state at 1.62 eV (≈ 1.75 eV), which corresponds to the <sup>3</sup>A<sub>2</sub> or the <sup>3</sup>E state, the deviation is somewhat larger

(0.4 eV). The experimentally determined excitation energies given by other authors also agree well with the theoretical results. It should however be noted that the experimental data vary somewhat (table 1) which is likely due to different oxide preparation techniques. The shifts of the surface states upon NO adsorption are also well reproduced. The calculated shifts seem to be slightly smaller than the observed ones. However, the  $\text{Ni}^{2+}$ -N distance is not well established yet [26,27]. If it is smaller than 2.38 Å which is the value for our calculations, slightly larger shifts will arise.

Table 2 indicates that not all of the existing surface states could be detected experimentally. For the  $^3\text{B}_2$  state the reason is that the energy of this state is quite near to that of the  $^3\text{T}_{2g}$  bulk state (see fig. 2) so that it cannot be separated experimentally from the  $^3\text{T}_{2g}$  loss. Concerning the other surface state it may only be speculated whether the loss is due to just one component, which might indicate that the other one has a weak cross section or whether it is a superposition of both components.

We wish to thank A. Gorschlüter and H. Merz for making ref. [11] available to us prior to publication. This work has been funded by the Deutsche Forschungsgemeinschaft (DFG) and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen. HJF gratefully acknowledges financial support by the Fonds der Chemischen Industrie.

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