Electronic surface states of CoO(100):
an electron energy loss study

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Abstract

We identify electronic excitations in the first layer of a CoO(100) surface applying electron energy loss spectroscopy. These excitations are localized within the optical band gap of CoO and correspond to excitations within the d orbital manifold of the Co^{2+} ions. The excitations of Co ions in the surface are different from those of Co ions octahedrally (sixfold) coordinated as in the bulk, because the ligand field at the surface is reduced due to the lower coordination (fivefold) at the surface. Two surface states can be identified in conjunction with ab initio calculations, one at 50 meV, i.e. below the Fuchs–Kliewer surface phonon, and another one at 0.45 eV below the first excited state of sixfold coordinated Co ions. The surface states are quenched upon gas adsorption.

Surface states of solids determine their electronic structure, and in turn many of their properties such as surface magnetism, adsorption behaviour, surface conductivity, etc. For metals such surface states have been identified very early. In 1967, the observation of a feature in field emission on W(100) was reported which was later on identified to result from an ionization out of a surface state [1]. Since then a large fraction of surface physics has been dedicated to the study of surface states, and there are still many activities in this field [2,3]. On non-metallic, e.g. transition metal oxide surfaces, on the other hand,

this topic has not received much attention to our knowledge [4]. This is surprising in view of the importance of ceramic materials in a variety of fields, including high temperature superconductivity, catalysis, device physics just to name a few. The experimental difficulties in combining non-metallic, and often non-conducting materials with electron spectroscopies may have been one class of reasons that hampered such studies. With the advent of thin film studies of non-conducting materials some of the problems have been circumvented [5]. The samples do not charge upon electron impact or emission and, even more importantly, the surfaces may be cooled to low temperature. This is particularly important in connection with the study of adsorbates. Adsorbates are rather crucial with respect to the identification of

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surface states because the 'crud test', i.e. the influence of adsorbed species on the intensity and energy position of surface states, can be used to identify such states [6].

We report in this Letter for the first time the identification of electronic excitations located in the first layer of a CoO(100) surface. One surface state has an excitation energy of 0.45 eV, the other one is situated in the range of the substrate phonons at 50 meV. Such a low lying electronic state has not been observed previously on any oxidic material. These surface excitations are probed with a standard electron energy loss spectrometer with a resolution of 8 meV [7]. The oxide surfaces have been prepared in two ways. Firstly, a bulk CoO single crystal has been cleaved along the (100) direction under ultrahigh vacuum conditions and the spectra have been recorded at room temperature where the conductivity is sufficient to avoid sample charging. Secondly, a thin CoO(100) film has been prepared via oxidation of a Co(1120) single crystal [8]. The layer was characterized via XPS measurements and its thickness has been determined to 10 Å [8]. The O 1s XPS line (not shown here) exhibited a shoulder at 1.5 eV higher binding energy indicating the presence of a very small amount of hydroxyl groups on the oxide surface. This is a common feature on oxide surfaces and is intimately connected with the defect structure of the film [9]. We know from previous studies that this has no influence on surface states of (100) orientation in the case of rock salt type structures [4].

Fig. 1 shows electron energy loss spectra of the CoO(100) surface as prepared, as well as after exposure to CO. In the upper panel a full scan over more than 1 eV loss energy is plotted. The low energy region is dominated by the very intense phonon structure, typical for oxide surfaces, and due to the efficient excitation of the Fuchs–Kliewer phonon series [10]. On the left hand side of the elastically reflected peak a gain feature can be clearly observed. The Fuchs–Kliewer losses stretch out to about 0.3–0.4 eV excitation energy with their intensity following a typical Poisson distribution. Between 0.4 and 1.2 eV we find three broader features, two of which are connected with electronic excitations, the one narrow peak at 0.45 eV is due to the excitation of the stretching vibrations of adsorbed OH [9]. We will show further below on the basis of ab initio calcula-
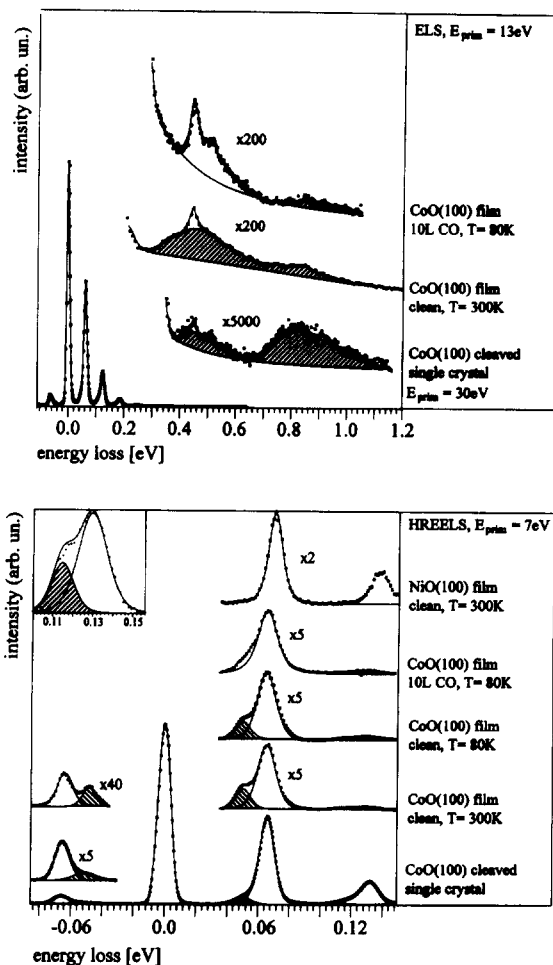

Fig. 1. Electron energy loss spectra of CoO(100). Upper panel: full range up to a loss energy of 1.2 eV; Lower panel: close up of the range up to 145 meV. The inset shows a fit of the high energy Fuchs–Kliewer feature based on the assumption of a combination mode.

tions that the feature between 0.7 and 1.1 eV contains contributions from bulk excitations as well as from surface excitations, while the broad feature peaking at 0.45 eV is due exclusively to a surface excitation. In addition to these surface states at higher excitation energies the ab-initio calculations also predict a further surface state at about 50 meV as will be discussed below. The lower panel of Fig. 1 shows an expanded view of the loss spectrum in the neighbourhood of the elastic peak and the primary Fuchs–Kliewer phonon loss and the corresponding gain features for cleaved CoO, a thin CoO film as

prepared and after adsorption of CO. Here a shoulder in the Fuchs–Kliewer loss towards lower energy in CoO can be clearly identified, while there is no such feature in the case of NiO(100) (see Fig. 1) [11]. Also, OH or water cannot be responsible for this signal because on CoO(111), the feature is missing, even though the OH concentration is higher [8]. The shoulder therefore indicates the presence of an additional excitation in CoO in this energy range which is corroborated by the spectra taken on the thin film. Due to the limited thickness of the CoO(100) film, the intensity of the Fuchs–Kliewer phonons is attenuated considerably [10], thereby decreasing the relative intensity of the phonon losses with respect to the additional feature, which is localized in the surface and characteristic for the topmost layer. The relative intensity for the extra feature becomes most prominent for the gain peaks because here the Boltzmann factor favors the state with lower energy and one can undoubtedly see the relative increase for both the cleaved surface and the film. We note at this point that the relatively high intensity of the electronic excitation at 50 meV could be caused by intensity borrowing from the phonon peaks.

The feature between 40 and 80 meV containing the shoulder may be fit by a linear combination of two Gaussians. The same is true for the higher energy features (e.g. between 100 and 140 meV). Via the fitting procedure the intensities of the various components may be determined. It is very well known [10] and accepted that the intensities of the phonon excitations follow a Poisson distribution. If we plot the intensities of the intense components of the features we find a typical Poisson behaviour as expected (not shown). On the other hand this is not observed if we plot the intensities of the weaker features indicating that these features have different origin. In fact, the weak feature at 115 meV may be fit perfectly by assuming that it is a combination mode between the excitation at 50 meV and the Fuchs–Kliewer phonon at 65 meV. An inset in Fig. 1 shows a simulation where the intensity of the signal at 115 meV has been determined by multiplying the intensities of the signal at 50 meV and the Fuchs–Kliewer phonon. If the intensity of the signal at 115 meV followed a Poisson distribution, it would be of about half the size.

In order to prove that some of the spectral fea-

tures are due to surface excitations we have exposed the surface to a gas which sticks to the surface at the given temperature. It is clearly shown in both panels of Fig. 1 that those states due to surface excitations are quenched upon CO adsorption indicating, indeed, localization in the surface.

The assignment of the spectra is based on ab initio calculations using a cluster model for the oxide surface [4,12]. We have chosen a cluster consisting of one Co^{2+} ion and six (for bulk CoO) or five (for the surface) neighboring O^{2-} ions, embedded in an infinite (bulk) or semiinfinite (surface) Madelung field of point charges ($\pm 2e_0$). The octahedral symmetry and the bulk Co–O distance of 2.13 Å [13] were fixed throughout the calculations. The ^4F ground state of Co^{2+} ($3d^7$) is split in the octahedral ligand field into a $^4T_{1g}$ ground state with the occupation $t_{2g}^5 e_g^2$ and two excited states $^4T_{2g}$ and $^4A_{2g}$. At the surface the threefold spatially degenerate states $^4T_{1g}$ and $^4T_{2g}$ are further split due to the reduced symmetry (C_{4v}) of the local environment of the surface Co^{2+} ion.

Our present ab-initio calculations have been performed as follows: First, a CASSCF calculation has been carried out for an energy expectation value averaged over all seven states of the ^4F manifold. These orbitals were then used for valence CI calculations in which either only the 3d atomic orbitals of Co^{2+} (VCI(d)), or the 3s,3p,3d atomic orbitals of Co^{2+} (VCI(spd)), or the 3d atomic orbitals of Co^{2+} and the 2p orbitals at the O^{2-} ions were included. Finally, dynamic correlation effects were incorporated by means of MC-CEPA (multi-configurational CEPA) calculations in which the 3d atomic orbitals of the Co^{2+} were correlated. The Bochum open shell program package [14] was used throughout. Our best MC-CEPA results for the lowest d–d excitation energies of Co^{2+} in different surroundings are shown in Fig. 2.

The splitting of the ^4F ground state of isolated Co^{2+} into $^4T_{1g}$, $^4T_{2g}$ and $^4A_{2g}$ in a purely electrostatic field (point charge model) is quite small (0.3 and 0.6 eV) and is considerably enhanced if the next coordination shells around the Co^{2+} ion are explicitly included, because of the strong Pauli repulsion between the Co 3d electrons and the O^{2-} ions. Our best results (CoO_6^{10} cluster + 18 effective core potentials (ECPs) for the next shell of positive ions + point
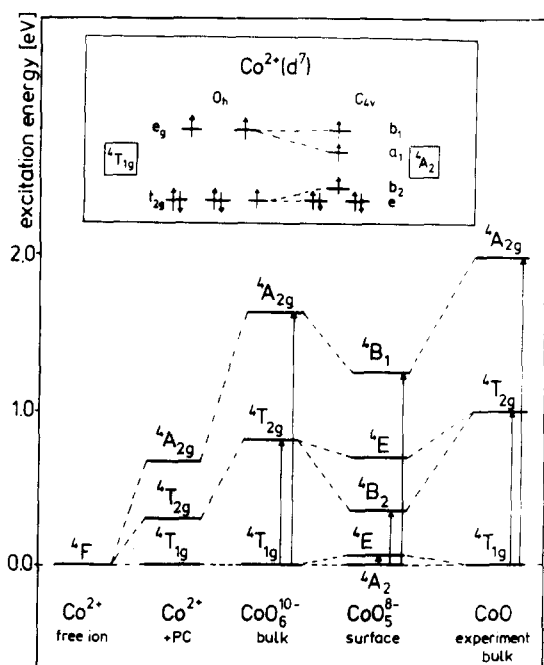
Fig. 2. Correlation diagram for excitation energies of a Co^{2+} ion in different coordination environments.

charges) at 0.8 and 1.7 eV are a little lower than the observed bulk peaks at 0.85 and 2.0 eV [15].

For a Co^{2+} ion at the $CoO(100)$ surface the degeneracies of the e_g and t_{2g} orbitals are partly lifted. Fig. 2 shows a d-orbital diagram in the inset. The main effect is the lowering of the $3d_{z^2}$ orbital due to the reduction of the ligand field caused by the missing O^{2-} along the z direction (normal to the surface). The $3d_{xz}$ and $3d_{yz}$ orbitals are only slightly stabilized with respect to the octahedral coordination. Parallel to the orbitals, also the degeneracies of the $^4T_{1g}$ and $^4T_{2g}$ states are partly lifted at the $CoO(100)$ surface: the ^4E state, split off from the $^4T_{2g}$ state, which is the one connected with the excitation of an electron from the e/b_2 set to the b_1 orbital is only moderately stabilized to 0.7 eV. However, the $^4B_2$ state is lowered to 0.35 eV because it is connected with the excitation of an electron from the e/b_2 set to the a_1 orbital. With a similar argument the lowering of the $^4B_1$ state ($^4A_{2g}$ in O_h symmetry) can be rationalized. The $^4T_{1g}$ ground state is split into a $^4A_2$ and a ^4E component. Here the splitting is determined by the fluctuation of the hole within the e/b_2 set leading to a very small energy

difference which is in the range of phonon excitations. It is calculated to be about 50 meV. As may be seen from Fig. 2 the results of our MC-CEPA calculations reproduce our experimental data both for bulk CoO and the clean $CoO(100)$ surface within about 0.2 eV. It cannot be excluded purely on the basis of the calculated results, however, that the $^4T_{1g}$ ground state of Co^{2+} in bulk CoO is split by spin–orbit coupling. On the other hand, the high surface sensitivity of the peak at 50 meV clearly indicates that it corresponds to a surface excitation, corresponding to the $^4E \leftarrow {}^4A_2$ energy difference, and not to a fine structure component of the $^4T_{1g}$ state in bulk CoO. The excitation energies experimentally determined by other authors [15] for the bulk transitions also agree with the theoretical results. It should however be noted that experimental data vary somewhat due to different oxide preparation techniques. A molecule bound to the $CoO(100)$ surface at the Co^{2+} site will – at least partly – fill the vacancy of the missing O^{2-} ion and strengthen the ligand field in the z direction. Therefore those states which were shifted to lower excitation energy due to the absence of the sixths ligand are now shifted back more or less close to the excitation energy in the bulk. Experimentally this is equivalent to a quenching of the surface excitation upon bonding of a molecule to the oxide surface.

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