# Electron-Exchange Processes in the Excitations of NiO(100) Surface *d* States

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Electron exchange processes in *d*-*d* transitions of the $\mathrm{Ni}^{2+}$-surface ions in NiO(100) had been examined by "complete" spin-polarized electron-energy-loss spectroscopy. Surface and bulk excitations show a completely different scattering geometry dependence, providing the possibility to distinguish between them. Besides the well-known 0.6 eV surface state, the loss structure at 2.1 eV excitation energy was identified as surface excitation. By use of the resonance primary energies, a new excitation at 1.3 eV was found, which was assigned to the $^3B_1 \rightarrow {}^3A_2$ surface excitation. [S0031-9007(96)00936-2]

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Electronic surface states are responsible for a variety of surface properties of solids, and in particular their influence on adsorbates might determine catalytic processes at the surface. Therefore, the catalytic behavior of the simple transition-metal monoxides like NiO and CoO led to intense experimental and theoretical investigations in the 3*d* states of the surface transition-metal ions of these materials [1–4] and related compounds [5]. We now present an examination of the electron exchange processes in the excitation into the surface *d* states of NiO(100) by means of "complete" spin-polarized electron-energy-loss spectroscopy (C-SPEELS). The behavior of electron exchange in the excitation of the bulk *d*-*d* transitions has been shown in previous papers [6–8].

In NiO, the eight electrons in the incompletely filled 3*d* shell of the $\mathrm{Ni}^{2+}$ ions are localized at the ion; they behave similar to the electrons of free atoms or ions and cannot be described in a band picture. Most suitable for their describtion seems to be a cluster model, where the bulk Ni ions are considered in the crystal field of the surrounding six $\mathrm{O}^{2-}$ ions, enbedded in an infinite Madelung field of point charges. At the surface, one $\mathrm{O}^{2-}$ ion is assumed to be missing and the clusters contain only five $\mathrm{O}^{2-}$ ions in a semi-infinite point charge Madelung field. The $O_h$ symmetry of the bulk NiO is reduced to $C_{4v}$ symmetry at the surface [1]. In contrast to the conditions at free ions or atoms, the degeneracy of the *d* states concerning $m_l$ is partially lifted, because $t_{2g}$ and $e_g$ states are energetically separated due to the crystal field. For example, the $^3F$ ground state of the free *d* configuration splits into three states, the $^3A_{2g}$ ground state and two excited states, $^3T_{2g}$ and $^3T_{1g}$, approximately 1.1 and 1.6 eV higher in energy. At the surface, the remaining degeneracy is further lifted, because the change in the crystal field, caused by the missing oxygen ion in the *z* direction (surface normal), affects mainly the *d* orbitals with *z* component, especially the $3d_{z^2}$ orbital. Whereas the $3d_{xy} \rightarrow 3d_{x^2-y^2}$ excitation energy remains nearly unchanged, the $3d_{xz} \rightarrow 3d_{z^2}$ and $3d_{yz} \rightarrow 3d_{z^2}$ excitations are energetically lowered, leading to a splitting of the $^3T_{2g}$-bulk excited state into a $^3B_2$ and a $^3E$ state at the surface. The excitation energies from the surface-ion ground state ($^3B_1$) into these states have been calculated to be 1.0 and 0.65 eV, respectively. The $^3T_{1g}$ state theoretically splits into a $^3A_2$ and a $^3E$ state of 1.3 and 1.44 eV excitation energy [1]. Except for the $^1S$ state, all excited states of the free *d* configuration ($^1D, {}^3P, {}^1G$) are also split in the crystal field, so that a manifold of excited *d* states of singlet as well as triplet character exists [1,9–11]. A further splitting of these states at the crystal surface, like described above for the ground state, must be assumed. Experimentally, a variety of *d*-*d* excitation energies have been determined [1,2,6–8,10], and most of it could definitely be attached to a certain calculated bulk-ion *d*-*d* transition. But up to now only the transition of about 0.6 eV excitation energy has been identified as surface-ion excitation ($^3B_1 \rightarrow {}^3E$ of $^3T_{2g}$) unambiguously by electron-energy-loss spectroscopy at clean [1,2] and NO-covered surfaces [1].

Normally, transitions between *d* states are forbidden by electric dipole selection rules, the triplet-triplet transitions by the parity selection rule ($\Delta l = \pm 1$) and the triplet-singlet transitions by the spin selection rule ($\Delta s = 0$) additionally. In the crystal field, the parity selection rule is slightly released, because the cubic symmetry of the Ni-O clusters is distorted by lattice vibrations. These vibrations lead to an admixture of the even parity *d* states with odd parity states, resulting in a nonvanishing matrix element of the electric dipole moment [11]. But, nevertheless, the transition probabilities remain small, leading to very small intensities in optical absorption spectroscopy [10]. Predestined for the examination of *d*-*d* transitions is the excitation by low energy electrons due to the possibility of electron exchange in the excitation process. In addition, the application of low energy electrons of 35–100 eV is especially suitable for the examination of surface ion *d*-*d* transitions, because of their low, in this energy range slowly varying, penetration depth into the solid [12]. The only possibility for unambiguous proof of electron exchange in nonferromagnetic materials is that kind of spin-polarized electron-energy-loss spectroscopy, where a polarized primary beam is scattered at the target,

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energy *and* polarization of the scattered electrons are measured. We call this method C-SPEELS to distinguish it from the more simpler SPEELS types of experiments, which use either spin-polarized primary electrons *or* polarization analysis of the scattered ones. Knowledge of primary and scattered electron polarizations, $P_0$ and $P_s$, in addition to the intensity curve $I(E)$, provides the spin-flip and nonflip intensities, $F$ and $N$, of the scattered electrons [6,8]. A change of $P_s$, resulting in a nonzero spin-flip intensity, is a direct check of electron exchange, if other spin-dependent interactions are negligible.

The experimental setup has been described in detail elsewhere [6]. To summarize, we use a conventional GaAs source with spherical 180° monochromator. In the measurements shown below, the primary beam polarization was $P_0 = (23 \pm 0.5)\%$ and the current impinging onto the target was about several hundred nanoamperes. The scattered electrons are energetically analyzed by a 180° spherical analyzer (acceptance angle 1.5°), identical to the monochromator; polarization analysis is done by a high energy (100 kV) Mott detector. The energy resolution, measured as FWHM of the elastically scattered electrons, is 230 meV. The scattering angle, given by the angle between the axes of the electron optics, is fixed to 90°. The scattering geometry is changed by rotating the sample, which alters incident and outgoing angles likewise; the [10]-direction of the surface Brillouin zone always remains in the scattering plane. To avoid charging, the NiO samples were heated to 100–150 °C during the measurements via heat conduction from a heating element, consisting of bifilar windings of tantalum wire.

Surface *d*-*d* excitations are visible only at freshly cleaved surfaces [2] or freshly prepared oxide films on Ni(100) [1], because the loss energies, attributed to certain *d*-*d* excitations, depend strongly on the crystal field [1–5] and therefore on the stoichiometry. The 0.6 eV energy loss, for example, occurs if the $\mathrm{Ni}^{2+}$ ions are surrounded by five $\mathrm{O}^{2-}$ ions exactly, like mentioned above. Therefore, all measurements shown below have been obtained at *in situ* cleaved commercial NiO(100) single crystals [2]. Up to the bulk Néel temperature of 523 K, they showed the typical four half-order low-energy electron diffraction spectroscopy spots, indicative for a multidomain antiferromagnetic surface [13].

It has to be noted that the surface stoichiometry is altered by electron impact, even at the low primary electron energies of about 30–40 eV. Just after 24 h of electron impact onto the same spot of the surface, the spectra begin to change slightly. Reproducible measurements are possible for a few days after cleavage, if the target position is changed with regard to the incident electron beam. Because of the shortness of available time after cleavage in connection with the usually very low counting rates in C-SPEELS of dipole-forbidden excitations, measurements at evaluated primary energies, energy losses, and scattering geometries are possible only. Here one can take advantage of the previously found resonance primary energies: Bulk as well as surface *d*-*d* excitations are resonantly enhanced at primary energies around 30, 38, and 100 eV, like earlier results [2,7,8] and our recent measurements at freshly cleaved surfaces show. All measurements reported below had been carried out at 38 eV primary energy, because especially at this energy all *d*-*d* excitation peaks reach their maxima and the highest change in electron polarization during the scattering process, caused by spin-flip exchange processes, was found for the bulk *d*-*d* excitations previously [7,8].

In Fig. 1, spin-integrated energy-loss spectra are shown for different scattering geometries. The *d*-*d* excitations appear as relatively sharp energy-loss peaks (A–G) in the band-gap region ($E_{\mathrm{gap}} > 3.2$ eV [14–16]), which reach their highest intensities in specular scattering geometry [Fig. 1(a)]. Near specular scattering geometry, the *d*-*d* transitions of higher excitation energies [F, G in Fig. 1(d)] are not visible, because they are strongly superposed by dipole-allowed transitions across the band gap. The scattering geometry behavior of the dipole-forbidden *d*-*d* excitations is quite different for surface and bulk ions. The intensity of the 0.6 eV surface excitation (peak A) is dramatically reduced by varying the angle ±2° only around specular geometry [Fig. 2(a)]. Whereas it increases against more grazing detection angles again, no indication for a further ascent toward more grazing incidence

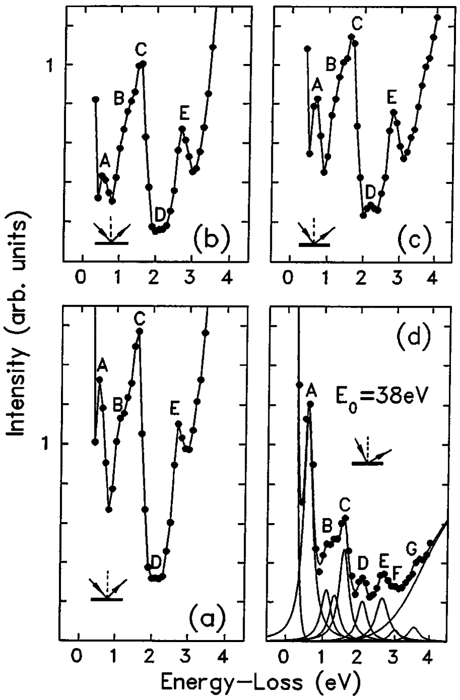

FIG. 1. Spin-integrated energy-loss spectra obtained at 38 eV primary energy for different scattering geometries. (a) Specular; $\theta_i = \theta_e = 45°$; (b) $\theta_i = 47.5°$, $\theta_e = 42.5°$; (c) $\theta_i = 37.5°$, $\theta_e = 52.5°$; (d) $\theta_i = 27.5°$, $\theta_e = 62.5°$. The continuous line in (d) is the addition of the fits in the lower part of the figure. *d*-*d*-excitation peaks were fitted by Lorentz profiles.

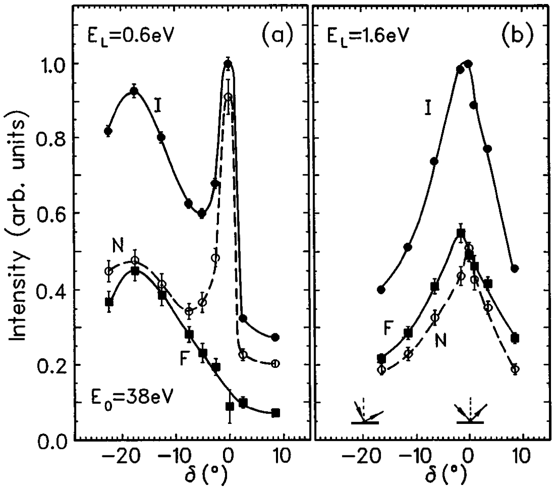

FIG. 2. Scattering geometry dependence of spin-integrated intensity $I$(●), spin-flip intensity $F$(■), and nonflip intensity $N$(○). (a) 0.6 eV (A) energy-loss ($^3B_1 \rightarrow {}^3E$ surface-ion excitation). (b) 1.6 eV (C) energy-loss ($^3A_{2g} \rightarrow {}^3T_{1g}$, $^1E_g$ bulk-ion excitation). $\delta$ is the deviation from specular scattering geometry, $\theta_i = 45° + \delta$, and $\theta_e = 45° - \delta$.

and steeper detection has been found. In contrast to this behavior, the intensity of the dominant 1.6 eV bulk loss feature (peak C) decreases much slower and nearly symmetrically to the specular scattering geometry [Fig. 2(b)]. This angular behavior was previously found to be typical for this bulk transition, excited by electrons of the resonance primary energies [8]. The polarization behavior of the scattered electrons is also completely different for the 0.6 eV surface and 1.6 eV bulk ion *d*-*d* transition. The excitation of the 1.6 eV transition leads to a quasi-complete, nearly scattering geometry independent depolarization of the scattered electrons (Fig. 3), interpreted by the formation and decay of a temporarily formed compound state [8]. Spin-integrated intensity, spin-flip, and nonflip intensities [Fig. 2(b)] increase nearly likewise toward specular scattering geometry, which leads to the conclusion of a mainly exchange dominated scattering process, even in specular scattering geometry [8]. For the 0.6 eV surface-ion excitation, the situation is quite different. Here, the polarization of the scattered electrons is high in specular scattering geometry (Fig. 3) and only slightly different to the polarization $P_0$ of the incident electrons. It is strongly dropped, if the specular geometry is left. The behavior of the spin-flip and nonflip intensities at 0.6 eV energy loss differs also strongly from that of the 1.6 eV bulk loss. The spin-flip exchange process, represented in the spin-flip intensity, increases toward grazing detection as well as nonflip and spin-integrated intensities [Fig. 2(a)]. The high amount of intensity, occurring in the small angular region around specular scattering geometry, lies in the nonflip intensity exclusively. It is not reflected in the spin-flip intensity at all and must therefore be attributed to nonflip direct scattering. The very small angular distribution is in accordance with the assumptions about dipole scattering, which is expected to occur in a small angular lobe around specular geometry only [17,18]. In fact, the dipole allowed transitions across the band gap, which appear in the nonflip intensity only [7], show an identical reduction in the same small angular region. Therefore, we conclude that the probability for dipole-allowed transitions is enhanced for the surface *d*-*d* excitations. The parity selection rule might be further released, because of the disturbance of the central symmetry at the site of the $Ni^{2+}$-surface ion due to the missing oxygen.

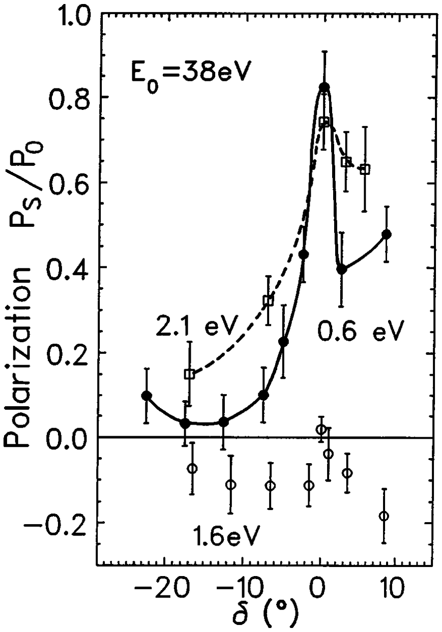

FIG. 3. Scattering geometry dependence of the polarization $P_s/P_0$ in the 0.6 eV (●), 1.6 eV (○), and 2.1 eV (□) energy-loss peaks (A, C, D).

The weaker loss structure at 2.1 eV (peak D) exhibits the same behavior as the 0.6 eV surface energy-loss peak, contrary to that of the 1.6 eV bulk loss peak. Its intensity increases toward grazing detection angles (Fig. 1). Therefore, the surface-excitation character of this loss peak must be assumed. It might be assigned to the excitation into a surface component of the $^1T_{2g}$ state (2.7 eV bulk excitation energy), probably the $^3B_1 \rightarrow {}^1E$ transition. The calculated excitation energy lies close to the measured energy of 2.1 eV [19]. In addition to the coincidence of the intensity dependence of the 0.6 and 2.1 eV energy-loss features, the polarization behavior of the 2.1 eV excitation corresponds to that of the 0.6 eV excitation (Fig. 3). But it has to be noted that the polarization values of the 2.1 eV peak are not as certain as those of the 0.6 eV loss, because, especially in specular scattering geometry, the 2.1 eV excitation is strongly superposed by the flanks of the 1.6 and 2.7 eV loss peaks and the onset of dipole-allowed transitions across the band gap, like curve fits show. The superposition of the 0.6 eV peak with neighbor loss peaks and especially the flank of the elastically scattered electron peak was found to be negligible.

As mentioned above, all *d*-*d* excitation peaks reach their highest intensity at the resonance primary energy of 38 eV. Off-specular, dipole-allowed transitions into defect states or across the band gap are more strongly reduced than the exchange excited *d*-*d* transitions, according to the angular dependence of dipole scattering [17,18]. This knowledge was used to determine a great number of *d*-*d* excitation energies by fitting the excitation peaks with Lorentz profiles [Fig. 1(d)]. Besides the transitions of 0.6, 1.6, and 2.1 eV energy loss discussed above, the well-known [2,9,10] bulk-ion *d*-*d* transitions at 2.7, 3.0, and 3.55 eV are reproduced. However, it has never been observed before that the well-known transition around 1.1 eV excitation energy consists of two components at 1.1 and 1.3 eV. We assign the 1.1 eV peak to a superposition of the $^3A_{2g} \rightarrow {}^3T_{2g}$ bulk-ion excitation with the $^3B_1 \rightarrow {}^3B_2$ surface-ion excitation and the 1.3 eV peak to the $^3B_1 \rightarrow {}^3A_2$ surface-ion excitation, predicted theoretically. The excitation energies lie very close to the calculated values [1]. The participation of surface ions in these excitations can be supposed, because the splitting is clearly visible in scattering geometries only, where bulk excitations are reduced and surface excitations are enhanced. Detailed investigations in the scattering geometry dependence of intensity and polarization to show the coincidence of the behavior of the two peaks with the other surface-ion excitation assigned peaks are impossible, because of their superposition and the strong superposition with the 1.6 and 0.6 eV peaks [Fig. 1(d)].

Summarized, “complete” spin-polarized electron-energy-loss spectroscopy is an efficient tool to distinguish between *d*-*d* excitations at bulk and surface Ni ions, because of the different scattering geometry dependence of the electron exchange processes. Taking advantage of this fact and the knowledge of the primary electron energies, where the *d*-*d* excitations resonate, the energy-loss structure at 2.1 eV could be assigned to a surface *d*-*d* excitation and the theoretically predicted 1.3 eV surface transition has been found experimentally.

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