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Spin-flip low-energy electron-exchange scattering in NiO(100)

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Spin-polarized electron-energy-loss spectroscopy was applied to study electron-exchange processes in insulating NiO(100). Dipole-forbidden *d*-*d* excitations of the Ni^{2+} ion give rise to sharp gap structures in the energy-loss spectrum. Our measurements show strong spin-flip electron-exchange scattering in the excitations with 1.1- and 1.6-eV energy loss up to high primary electron energies of more than 100 eV. No spin-flip exchange scattering is found in the excitations leading to the loss structure around 2.8 eV.

INTRODUCTION

The existence and behavior of localized electronic states in insulating transition-metal (TM) oxides like NiO, CoO, or Cr_2O_3 have been of great interest for many years. Because of a strong Coulomb correlation, the electrons in the partially filled 3*d* shell of the TM ions in such compounds do not show bandlike, but quasiatomiclike character.[1-3] In contrast to free atoms, where the *d* states are energetically degenerate for different m_l, this degeneracy is partially lifted in the compounds by the crystal field. Electronic transitions between *d* states are strongly dipole forbidden for free atoms, but nevertheless, forbidden *d*-*d* transitions of Cr^{3+} impurities in Al_2O_3, for example, are used for the generation of laser light in the ruby laser.

Localized 3*d* states in NiO have been examined by optical-absorption measurements[4,5] and unpolarized electron-energy-loss-spectroscopy (EELS).[6-9,17] Because of its large band gap of more than 3.2 eV,[4,7,10] the dipole-forbidden *d*-*d* transitions of the Ni^{2+} ions appear as structures in the band-gap region of the spectra. Only the high-energy ones are superposed by a weak background of dipole-allowed transitions across the band gap. The gap structures are very weakly visible in optical-absorption measurements and their intensity only arises from electric dipole transitions, which become slightly allowed by ion-lattice interactions[4,11] and by a weak *p*-*d* hybridization.[12] In EELS with low-energy electrons, additional excitation by higher-multipole direct-scattering and by electron exchange is possible. But up to now, the role of electron exchange in the *d*-*d* transitions of NiO has been inferred only indirectly from the energy- and angle-dependence of the loss structures in EELS measurements.[6] If the primary energy is lowered to values comparable to the excitation energy and the scattering angle is large, the possibility of exchange with the target electrons increases.[13] Thus, loss structures mainly caused by electron exchange show an increasing intensity with decreasing primary energy. However, this behavior could also be caused by an energy dependence of the direct-scattering cross section.

For a direct experimental check of exchange processes, it is necessary to distinguish between the outcoming target electron and the scattered primary electron. This possibility is given in a "complete" spin-polarized electron-energy-loss experiment (C-SPEELS) only, where polarized electrons are scattered at the target and polarization and energy of the scattered electrons are analyzed simultaneously. Exchange can occur with or without spin flip, depending on the nature of the target excitations. Scattered primary and ejected target electrons are distinguishable in the former case if spin-orbit interaction is negligible—the polarization of the scattered electron beam changes in analogy to the amount of spin-flip exchange scattering.

It is known from C-SPEELS experiments with free atoms that exchange scattering can lead to a drastic depolarization of the scattered electrons, depending on the primary energy and the multiplicity of the participating initial and final states:[14] Singlet-singlet transitions are excited without spin flip only—the polarization of the electrons remains unchanged. Singlet-triplet or triplet-single excitations are possible by electron exchange only, if spin-orbit interaction is absent. As a consequence of transition probabilities, spin flips are more probable than nonflips in this case, which can lead to a reversal of the sign of polarization if the primary energy is comparable to the excitation energy.[13,14] Triplet-triplet transitions can be excited by electron exchange as well as by direct scattering (without exchange).

In NiO, the Ni^{2+} ions are octahedrally surrounded by O^{2-} ions, which provide a partial lifting of the degeneracy of the $3d^8$ states in the Ni^{2+} ions: The d_{z^2} and $d_{x^2-y^2}$ orbitals (e_g states) are energetically separated from the d_{xy}, d_{xz}, and d_{yz} orbitals (t_{2g} states). The ground state of the ions is of ${}^3A_{2g}$ symmetry ($t_{2g}^6e_g^2$), several excited states with triplet and singlet character have been predicted theoretically.[15-17] If the *d*-*d* excitations in a NiO crystal follow rules similar to free-atom excitations, spin-flip exchange scattering by slow electrons is expected in both the excitation from the triplet ground state to a singlet or triplet final state, but its quantity might be different. First C-SPEELS measurements on Cr_2O_3 showed a high amount of spin-flip exchange scattering in the excitation of *d*-*d* transitions.[18] In this paper, we report on C-SPEELS measurements on NiO.

EXPERIMENT

The experimental setup is described in Ref. 19. Longitudinally polarized electrons are generated by a GaAs source.[20] After a 90° deflection, where the polarization direction remains unchanged, the now transversely polarized electrons are scattered at the surface of a NiO(100) single crystal. Electrons, scattered at the fixed scattering angle of 90°, are energy analyzed by a spherical 180° deflector with resolution better than 250 meV. Measurements are taken in specular and in off-specular scattering geometry by rotating the sample. Spin analysis is done by a high-energy Mott detector (100 keV). The incident-beam polarization P_0 is measured by applying a repulsive potential to the target, so that the electrons reach the Mott detector without interaction with the target atoms. P_0 varied between 20–30 %, depending on the quality of the GaAs crystal used.

The NiO crystals were initially cleaved *in situ* along the (100) plane and then prepared by repeated sputtering with 500-eV argon ions. Because of the low counting rate due to spin-polarization analysis of inelastically scattered electrons with energy loss arising from dipole-forbidden excitations, the measuring time needed to obtain sufficiently small statistical errors was too long to use cleaved, not sputtered surfaces only. Differences to spectra obtained on freshly cleaved crystals are discussed below. During sputtering and during the measurements, the NiO crystals were heated to 100 °C to avoid charging effects.

RESULTS AND DISCUSSION

Figure 1 shows two spin-integrated energy-loss spectra of the sputtered NiO(100) surfaces, measured off-specular 1(a) and in specular scattering geometry 1(b), together with one obtained on a freshly cleaved surface in specular geometry 1(c).[6] All spectra were taken with 100-eV primary energy. The dipole-forbidden *d*-*d* transitions give rise to the gap structures (*A*–*E*); the strong increase in intensity above 3-eV energy loss is caused by dipole-allowed transitions across the band gap. Shape and energy positions of the bulk *d*-*d* transition-assigned structures at 1.1-, 1.6-, and around 2.8-eV energy loss (*B*,*C*,*E*) are nearly identical in both kinds of preparation. However, the gap structures are more visible in the spectrum of the freshly cleaved surface, because a continuous background due to sputter-induced defects is absent. The peak at 0.6-eV energy loss (*A*) is absent in the spectra of the sputtered surface, which supports the hypothesis that this structure is caused by a surface *d* state,[6] which presumably does not exist at sputtered surfaces. At smaller incidence angle [Fig. 1(a)] the overall intensity is decreased, but the shape of the spectrum remains nearly the same, except for an increase in relative intensity of the structure at 1.1 eV (*B*).

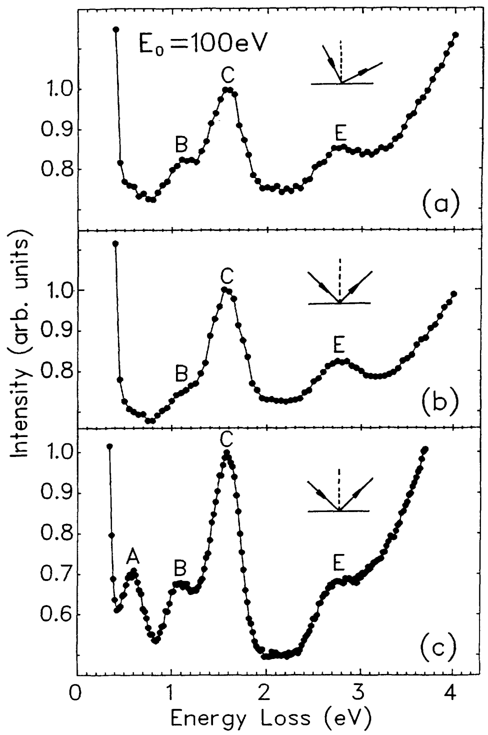

FIG. 1. Spin-integrated electron-energy-loss spectra for 100-eV primary energy, obtained on sputtered (a), (b), and UHV-cleaved NiO(100) surfaces (c) (Ref. 6). The scattering geometry is given in the insets. (a) $\theta_i=25°$, $\theta_e=65°$, (b) and (c) specular geometry.

Figure 2(a) shows the spin-integrated energy-loss spectrum at 20-eV primary energy in off-specular geometry ($\theta_i=25°$, $\theta_e=65°$). Compared to the energy-loss spectrum at 100-eV primary energy obtained with the same scattering geometry [Fig. 1(a)], the intensity ratio of the structures at 1.6 (*C*) and 2.8 eV (*E*) has changed. This is interpreted by a different energy dependence of the cross sections for these excitations and by the resonant enhancement of the *d*-*d* excitations at about 100-eV primary energy, where the 1.6-eV loss is favored.[6] At small energy losses, the intensity increases strongly, forming an "intensity tail" at the low-energy side of the elastically scattered electron peak. In the spectra taken at 100-eV primary energy, this tail is not present (Fig. 1) and it is much less marked in measurements obtained on UHV-cleaved, unsputtered surfaces, even at low primary energy.[6] Crystal defect states caused by sputtering might be responsible for this ascent. Probably, the cross section for the excitation in these states is energy dependent and lower at 100-eV incident energy. As a consequence the energy-loss structure at 1.6 eV (*C*) is superposed to a continuously increasing intensity background, the loss structure at 1.1 eV (*B*) appears as shoulder only. At about 2.1-eV energy loss, an additional weak structure appears (*D*). A structure at this energy loss was seen in an early optical absorption measurement with thin NiO films too,[4] but remained unexplained. Because this structure is usually not seen in spectra obtained at UHV-cleaved sur-

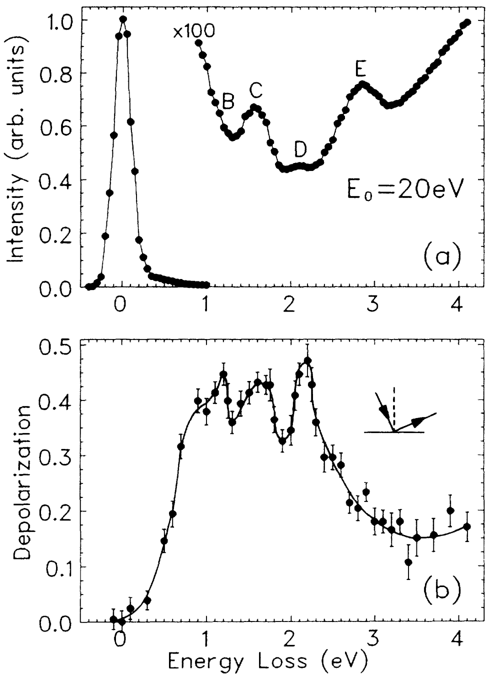

FIG. 2. Spin-integrated electron-energy-loss spectrum (a) and depolarization (b) for 20-eV primary energy, measured in off-specular scattering geometry.

faces,[6] we assign it to a localized defect state, caused by the sputter cleaning.

In C-SPEELS, the polarization of primary and scattered electrons is measured in addition to the spin-integrated intensity. This provides two further energy-loss spectra, the spin-flip spectrum $F(E)$ and the spin-nonflip spectrum $N(E)$. Additionally, we define the depolarization $D(E)$,

$$F(E)=0.5[1-P_S(E)/P_0]I(E) , \quad (1)$$

$$N(E)=0.5[1+P_S(E)/P_0]I(E) , \quad (2)$$

$$I(E)=F(E)+N(E) , \quad (3)$$

$$D(E)=1-P_S(E)/P_0 , \quad (4)$$

where P_0 is the primary electron polarization, $P_S(E)$ the polarization, and $I(E)$ the spin-integrated intensity of the scattered electrons.

Figure 2(b) shows that the depolarization is large for most excitations within the band gap; the maxima coincide with the d-d transition-assigned intensity maxima. The polarization of the elastically scattered electrons remains unchanged [$D(E)=0$ in the range of the elastic peak] which allows the conclusion that spin-orbit interaction between incoming electron and target is negligible. At energy losses larger than approximately 400 meV, the influence of elastically scattered electrons is already small and a considerable amount of transitions into the first excited Ni^{2+} state (maximum at 1.1 eV) is not yet expected, but the depolarization increases. Therefore, excitations into the continuously distributed defect states seem to be accompanied by spin-flip exchange scattering. The depolarization increases rapidly with increasing energy loss and reaches its first maximum at 1.1 eV. Despite the fact that the gap structure at 1.1 eV (B) is nearly invisible in the spin-integrated intensity spectrum at 20-eV primary energy, a distinct maximum is discernible in the depolarization. This indicates a high amount of spin-flip exchange scattering for this ${}^3A_{2g}(t_{2g}^6e_g^2)\rightarrow{}^3T_{2g}(t_{2g}^5e_g^3)$ assigned transition, as is expected for the excitation of triplet-triplet transitions by electron exchange. We note that this result is in contradiction to the interpretation of measurements at Cr_2O_3, where the equivalent multiplicity-conserving transitions from the ground state (t_{2g}^3 configuration) to excited states of $t_{2g}^2e_g$ or $t_{2g}e_g^2$ configuration are assumed to provide a nonflip background.[18]

The peak around 1.6-eV energy loss [Fig. 2(a)] consists of two overlapping structures, which are attributed to a ${}^3A_{2g}(t_{2g}^6e_g^2)\rightarrow{}^1E_g(t_{2g}^6e_g^2)$ and a ${}^3A_{2g}(t_{2g}^6e_g^2)\rightarrow{}^3T_{1g}(t_{2g}^4e_g^4,t_{2g}^5e_g^3)$ transition.[6,15,17] It appears in both the spin-flip and the spin-nonflip intensity (Fig. 3), showing clearly the high portion of exchange scattering at this energy loss. In contrast to the triplet-singlet transition, the triplet-triplet transition can be excited by direct as well as exchange scattering. Therefore, it could be expected that both transitions, which are not resolved in the spin-integrated spectrum, were resolved in the depolarization and spin-flip spectra because of a different amount of spin-flip exchange scattering. But a splitting is really not seen in these spectra. The reason might be an angular dependence of the different scattering mechanisms, similar to that known from theories and measurements at other materials:[13,21] Whereas the exchange scattering is angular wide spread and probably more effective at large scattering angles, the efficiency of direct dipole scattering is peaked around specular geometry. Therefore, in off-specular geometry, the scattering might be determined by exchange processes exclusively, even in the case of triplet-triplet excitations. In addition, another effect comes into play: It is known from optical-absorption measurements of ruby (Cr^{3+} in Al_2O_3) (Refs. 11 and 22) that the spin-forbidden, multiplicity-changing transitions lead to weak sharp lines, whereas the only parity-forbidden transitions give rise to strong broad structures in the spectra. The broadening of the lines is caused by vibrations of the Cr-O system during the exci-

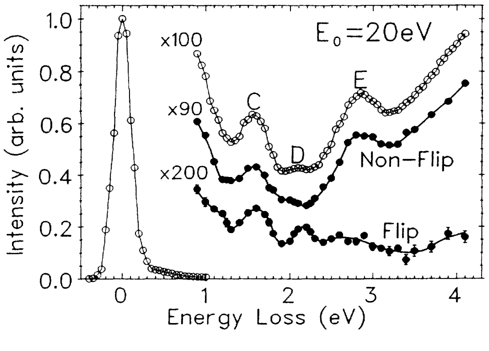

FIG. 3. Spin-flip (●) and nonflip intensity (●) for 20-eV primary energy, measured in off-specular scattering geometry. In addition, the spin-integrated intensity (○) from Fig. 2 is shown.

tation from the t_{2g} to the more antibonding e_g orbital, at which the bonding length changes. In the case of electron scattering, the intensity of the multiplicity-changing excitation might be enhanced due to exchange scattering, but the line shape is expected to remain unaffected. As inferred from the Tanabe-Sugano diagram for Ni^{2+} ions[11] a similar line behavior of the discussed triplet-triplet and triplet-singlet transitions in NiO is expected. Therefore, the loss structure around 1.6 eV might be dominated by the broad triplet-triplet excitation and differences in the quantity of spin flips in triplet-triplet or triplet-singlet transitions become invisible.

The depolarization [Fig. 2(b)] reaches its maximum at the extremely weak intensity structure [Fig. 2(a)] at 2.1 eV (D), which we assign to a localized defect state. Figure 3 shows that this structure appears in the flip intensity only—the nonflip intensity is nearly flat in this energy range. Because of this strong depolarization, we suggest that the excitation is mainly of triplet-singlet character.

Energy-dependent and spin-resolved measurements show spin-flip exchange scattering for the structures at 1.1- and 1.6-eV energy loss up to more than 100-eV primary energy (not shown here). This fact supports the interpretation of energy-loss measurements with unpolarized electrons on NiO, CoO, and rare-earth metals.[6,23] Exchange scattering is very effective in excitations between localized $3d$ or $4f$ states in solids, even if the primary energy is much higher than the energy loss. This is quite different from the observed behavior of exchange scattering at atoms, where exchange of s or p electrons is detectable for primary energies close to the excitation threshold only.[13,14]

In specular geometry (not shown in Figs. 2 and 3) the depolarization decreases drastically in our measurements. This effect is in accordance with the assumption about the angular dependence of the two scattering mechanisms involved in the excitation of triplet-triplet transitions as described above, i.e., the decreasing influence of exchange and a strong increase of direct scattering in this scattering geometry.

Surprisingly, the intense structure around 2.8 eV (E) shows quasi no depolarization [Fig. 2(b)]. It appears in the nonflip intensity only (Fig. 3), although theories predict excitations in some d states of singlet and triplet character[4,15,16] and angle- and energy-dependent EELS measurements show a similar behavior of the 2.8-eV peak like the other bulk d-d transitions.[6] The fact that this structure appears on a background of first dipole-allowed transitions across the band gap, which might be dominated by direct scattering, cannot explain this behavior sufficiently. However, the missing flip intensity does not necessarily imply the absence of exchange scattering at all. It must be noted that the structure is better visible in our measurements obtained at sputtered surfaces than in those measured at freshly cleaved ones[6] and the structure gained intensity during our first sputter cycles. This could be a hint of a strong superposition of the bulk d-d transitions by defect transitions at the same energy loss. If these transitions were dipole allowed and mainly caused by direct scattering mechanisms, the 2.8-eV peak might show no considerable flip-intensity and would appear in the nonflip intensity only. Here, C-SPEELS measurements on freshly cleaved NiO samples can clarify whether defect transitions or a particularity in the excitation between the participating d states, which might occur in systems with strongly correlated electrons, lead to the existence of nonflip intensity only.

SUMMARY AND CONCLUSIONS

C-SPEELS measurements at sputter-cleaned NiO(100) surfaces show that spin-flip exchange plays an important role in the excitations between localized $3d$ states of Ni^{2+} ions in NiO. The behavior of the electron depolarization at the 1.1- and 1.6-eV structures gives evidence for a high amount of triplet-triplet transitions. The weak structure at 2.1-eV energy loss, which we assigned to sputter-induced localized defects, showed mainly the character of a triplet-singlet excitation. For the structure around 2.8-eV energy loss no spin-flip exchange scattering was found, contrary to expectations from previous unpolarized EELS measurements. Spin-flip exchange scattering is detectable for NiO up to 100-eV primary energy, a value far above the excitation energies of a few electron volts. Therefore, the behavior of localized, atomiclike states in solids differs considerably from that of free atoms concerning electron-exchange scattering, which is significant only for primary energies in the vicinity of the excitation energy.

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