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LETTER TO THE EDITOR

## Long-range ferromagnetic order of Ni–O overlayers studied by quadrupolar resonant photoemission

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**Abstract.** The resonant photoemission decay from the Ni 2p x-ray absorption of ferromagnetic nickel can be decomposed into contributions from the monopole and the quadrupole moment of the core hole with substantially different signals for each of the final-state  $LS$ -terms. The quadrupole moment induces an anisotropic contribution to the photoelectron distribution which can be used to identify the different final-state  $d^n$  configurations in Ni and to separate substrate and overlayer signals on the Ni(110)-(3 × 1) O surface. The results provide evidence for a long-range ferromagnetic ordering in the Ni–O overlayer.

The oxygen-induced reconstruction of the Ni(110) surface has received much attention as an initial step in the formation of an oxide layer [1]. Magnetic properties of the reconstructed Ni–O overlayer are of interest in the study of electronic exchange interactions in low-dimensional systems. In bulk NiO the superexchange between the localized Ni 3d electrons mediated through the O ions leads to an antiferromagnetic ordering. For the Ni–O layer, normal exchange interaction via the Ni substrate is also possible, and should result in a ferromagnetic spin alignment in the overlayer. Experimentally, the question of the magnetic order in the Ni–O layer is not settled. Spin-polarized secondary-electron spectroscopy measurements [2] indicated the existence of several magnetically *dead* layers after O adsorption. Similar results were obtained for other systems [3, 4]. This could also indicate an antiferromagnetic surface order leading to the observed net spin polarization. Experiments with spin-polarized direct and inverse photoemission (PE) [5, 6] show exchange splitting of the adsorbate-derived bandstructure—indicating ferromagnetic order. However, the interpretation of the PE data relies on the separation of substrate and overlayer bandstructure which is ambiguous.

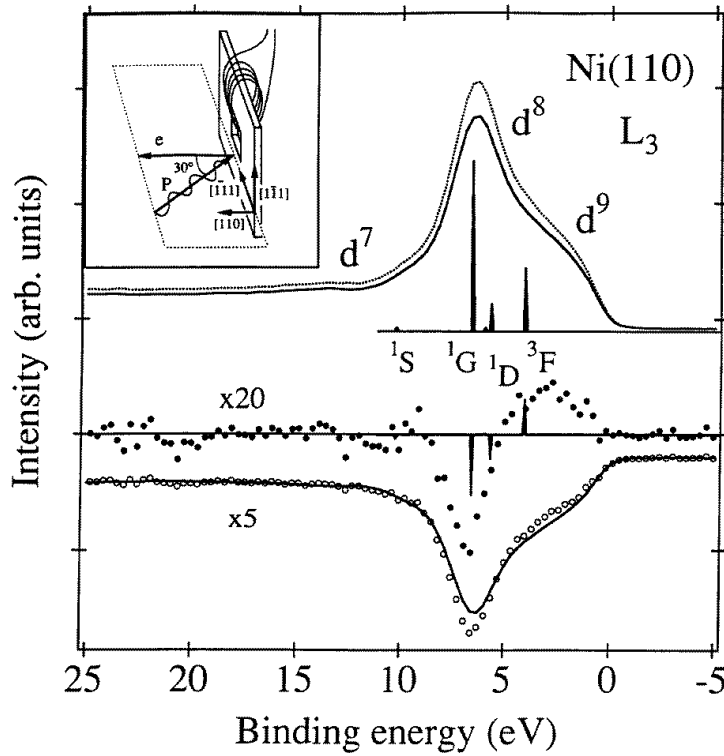
In this letter we show that it is possible to resolve the controversy by determining the energy position and spin polarization of the PE final-state  $d^n$ -like configurations. Ni is a prototype material since the reduced 3d orbital overlap—as compared to lighter 3d metals—causes an increased electron localization. This leads to an energy difference between the  $d^n$  configurations which depends on the on-site Coulomb interaction, the hopping integral and the band width of the 3d electrons. Ni metal has a predominantly  $d^9$  ground state with small  $d^{10}$  and  $d^8$  admixture. The low-lying  $^3F$  state of the  $d^8$  multiplet imposes a parallel spin alignment on adjacent Ni atoms which fluctuate between  $d^9 + d^9$  and  $d^{10} + d^8$ . In the electron-removal spectrum (valence band photoemission) the states near the Fermi level have mainly  $d^9$  character, and the  $d^8$  and  $d^7$  configurations, which are found at higher binding energy (BE), are split by electrostatic interactions into different  $LS$ -terms. Upon O adsorption some electronic charge is removed from the Ni atoms and the weight in

the ground state shifts towards lower d counts. Thus the  $d^7$  weight will increase in the photoemission spectrum.

The final-state  $d^8$  and  $d^7$  configurations are enhanced in the resonant photoemission decay. For the deep  $2p_{3/2}$  core level the resonant process is dominated by the autoionization decay following initial x-ray absorption  $3d^n \rightarrow 2p_{3/2}^5 3d^{n+1} \rightarrow 3d^{n-1} + e$  [7]. In principle this allows us to find the relative energy position of the  $d^8$  and  $d^7$  configurations with respect to the  $d^9$  configuration, but in practice the multiplet splitting makes it difficult to separate them from each other. An improvement is achieved by using magnetic circular dichroism. When in x-ray absorption spectroscopy (XAS) an electron from a spin-orbit-split core level is excited into a magnetic valence state the dipole selection rules together with the Pauli principle give a difference in absorption probability for the light polarization aligned parallel and antiparallel to the magnetization. Since the dichroic signals for  $2p_{3/2}^5 3d^{10}$  and  $2p_{3/2}^5 3d^9$  intermediate states are different, this will show up in the photoemission decay to the  $d^8$  and  $d^7$  final states, as has been observed by Tjeng *et al* [8]. The decay rate does not depend on the polarization of the core hole because this polarization influences the direction of emission but not the integrated photoemission *per hole* created. Therefore, just as in XAS using total electron yield, only the monopole of the core hole is measured. However, the polarization  $2p_{3/2}$  of a core hole in a 3d transition metal also contains a quadrupole term, which can be observed in the angular photoelectron dependence [9, 10]. Thus the isotropic photoemission decay spectrum,  $B^0$ , measures the monopole moment of the 2p core hole, whereas the anisotropic contribution in the photoemission decay spectrum,  $B^2$ , is a measure for the quadrupole moment of the core hole. Since the core-hole decay leads to different angular photoelectron distributions for each  $LS$ -term, the  $B^2$ -spectrum will have a uniquely different spectral lineshape from that of  $B^0$  [9]. We will show that this can be used to separate the Ni substrate and Ni-O overlayer  $d^n$  multiplets and establish a long-range ferromagnetic ordering in the overlayer on the Ni(110)-(3 × 1) O surface.

Experiments were performed on beamline 1.1 of the Synchrotron Radiation Source at Daresbury with 80% circularly polarized x-rays. The experimental geometry is shown in the inset of figure 1. Photoelectrons were detected using a hemispherical energy analyser mounted in the plane of the electron orbit at an angle of  $30^\circ$  with respect to the incoming photons. All spectra described in this letter were measured in the normal-electron-emission geometry. The Ni(110) substrate was a single crystal in the shape of a picture frame and magnetized along its in-plane  $[1\bar{1}1]$  easy axis by a current pulse through a coil. The surface was cleaned in the usual way by Ar-ion sputtering and annealing. Residual C contamination was removed by adsorbing O and subsequent annealing. The surface cleanliness was checked by x-ray photoemission spectroscopy and the surface order with low-energy electron diffraction (LEED). O was dosed at room temperature until the LEED showed a well ordered  $(3 \times 1)$  pattern corresponding to an O coverage of two thirds of a monolayer [1]. The clean Ni(110) surface is characterized by close-packed atomic rows along the  $[1\bar{1}0]$  direction. Perpendicular to that, along  $[001]$ , the lattice spacing is larger by a factor of  $\sqrt{2}$ . The Ni(110)-(3 × 1) O surface structure is well known and consists of almost linear Ni-O rows along the  $[001]$  surface direction. Every third Ni-O row is absent along the  $[1\bar{1}0]$  direction [1].

The upper part of figure 1 shows the photoemission spectra of the valence band region of clean Ni(110) in resonance with the  $2p_{3/2}$  ( $L_3$ ) absorption edge for the light helicity vector parallel (solid line) and antiparallel (dashed line) to the magnetization direction with an included angle of  $60^\circ$ . Since the intermediate state has predominantly  $2p_{3/2}^5 3d^{10}$  character at the  $L_3$ -edge maximum [8] the resonant enhancement  $3d^n \rightarrow 2p_{3/2}^5 3d^{n+1} \rightarrow 3d^{n-1} + e$



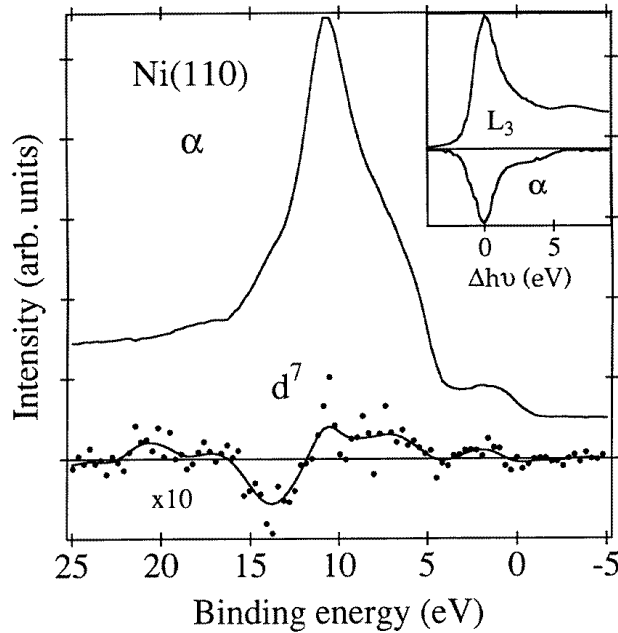
**Figure 1.** Valence band photoemission spectra of the Ni(110) surface measured at normal emission with the photon energy at resonance with the  $L_3$  absorption edge. The inset shows the experimental geometry. The spectra in the upper panel have been measured with the photon helicity,  $P$ , parallel (solid line) and antiparallel (dotted line) to the sample magnetization direction with an included angle of  $60^\circ$  between the two vectors. The lower panel shows the decomposition of the difference spectrum (open circles) into the contributions  $B^0$  (solid line) and  $B^2$  (solid circles). The  $B^0$ -spectrum is approximated as the sum of the two measured spectra from the top of the figure.

identifies final-state  $LS$ -terms of  $d^8$  character. For comparison the calculated  $LS$ -states assuming a pure  $d^9$  ground state (vertical bars) are given, showing a good agreement with the measurements.

The difference spectrum (open circles) is a superposition of the  $B^0$ - and  $B^2$ -spectra. Neglecting linear dichroism  $B^0$  can be approximated as the sum of the spectra for the two opposite magnetization directions. The result is shown as the solid line in the lower part of figure 1 which is normalized to the difference spectrum using the flat region above 20 eV BE. The difference between the two spectra gives  $B^2$  (solid circles). As a check we also made measurements for other geometries. The lineshape of  $B^2$  is identical to the one found in a geometry where  $B^0$  does not contribute, i.e. at normal light incidence [9]. We also obtained identical  $B^2$ -spectra for thin Ni films grown on Cu(100). There, however, the intensity is a factor of two larger. This is very probably due to multiple-electron-scattering effects which are different at (110)- and (100)-oriented Ni surfaces. We point out that the spectral lineshape is unaffected and agrees with a calculation assuming a pure  $d^9$  ground state (vertical bars in figure 1). The additional intensity near the Fermi level is due to the final-state  $d^{10}$  configuration, which is only assessable by direct photoemission

or interference with the  $d^9$  configuration. Figure 1 shows that in the  $B^2$ -spectrum the triplet states have positive intensity and the singlet states negative intensity. The spectrum, therefore, bears a resemblance to the spin difference spectrum, although in the latter the triplet states are smaller and singlet states larger. Thus the plus/minus structure of the  $B^2$ -spectrum provides an accurate way of determining the high- and low-spin states at low and high BE, respectively. This has been found for the other decay channels as well [9, 10].

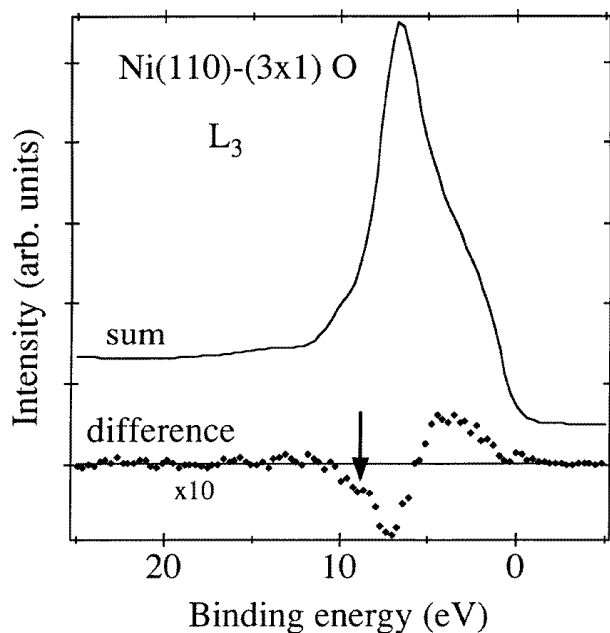
We also like to point out that the presence of the  $B^2$ -signal is contrary to the suggestion by López *et al* [11] that the strong enhancement observed in the valence band spectra at photon energies near the 2p absorption edge is mainly due to an incoherent superposition of a photoemission signal with a more intense LMM Auger signal. The latter would have no significant dichroism and also be present above the edge. We found that the  $B^2$ -signal is only present in the main peak and the XAS satellite structure. Additional evidence that we are really measuring resonant decay is that at the  $2p_{1/2}$  edge we are observing only a  $B^0$ -signal, which is in agreement with the fact that a  $j = 1/2$  level has no quadrupole moment [9].



**Figure 2.** Sum (solid line) and  $B^2$ - (solid circles) spectra for the Ni(110) surface with the photon energy 4 eV above the  $L_3$  edge. This photon energy coincides with the satellite  $\alpha$  in the difference spectrum in x-ray absorption (shown in the inset along with the averaged absorption spectrum). The solid line through the  $B^2$ -spectrum data points is a smoothed curve to guide the eye.

To determine the final-state  $d^7$  configuration we choose a photon energy of 4 eV above the  $L_3$  edge, where the satellite in the XAS difference spectrum (peak  $\alpha$  in the inset of figure 2) has predominantly  $2p_{3/2}^5 3d^9$  character [8, 12]. Performing the same decomposition procedure as above, we obtain the lineshape for the  $B_2(d^7)$ -spectrum (solid circles in figure 2), which shows a plus/minus structure similar to that of the  $B^2(d^8)$ -spectrum but is spread out over a wider energy range. Thus, the multiplet structure is much broader in this case. The structure is also shifted towards higher BE by 6.5 eV in agreement with earlier results

[8]. The positive intensity of  $B^2(d^7)$  at a binding energy of around 7 eV, i.e. at the position of the maximum of  $B^2(d^8)$ , indicates a mixing between the final-state  $d^7$  and  $d^8$  configurations. This mixing is, however, far less pronounced than that between the final-state  $d^8$  and  $d^9$  configurations (cf. figure 1) caused by the larger energy separation. If, for instance due to the charge transfer from Ni to O, the energy separation between the  $d^7$  and  $d^8$  configurations was reduced, one would expect to observe a stronger mixing.



**Figure 3.** Sum (solid line) and  $B^2$ - (solid circles) spectra for the O-reconstructed Ni(110) surface with the photon energy in resonance with the  $L_3$  edge. The arrow highlights the additional quadrupole feature associated with the Ni atoms bonded to oxygen.

The latter seems to be the case on the oxygen-covered surface. Figure 3 shows that the shape of  $B^2(d^8)$  changes on the high-BE side as compared to that for the clean Ni(110) surface. Most pronounced is an additional shoulder at 9.5 eV BE, which is clearly above the noise level. Its position with respect to the  $B^2(d^8)$ -spectrum of clean Ni(110) strongly suggests that it is due to the final-state  $d^7$  configuration. Another difference from the clean Ni(110) spectrum is the higher intensity for  $B^2$  in figure 3. This is most probably a consequence of the surface reconstruction leading to a change in diffraction of the outgoing photoelectron wave. As shown above this cannot explain the additional shoulder at 9.5 eV BE. The lineshape change is, therefore, caused by a quadrupolar core-hole decay localized on the overlayer Ni atoms. This is direct proof of long-range ferromagnetism in the overlayer. If a significant fraction of the overlayer Ni atoms were ordered antiferromagnetically or were magnetically *dead* the net circular dichroism signal would be much smaller.

We can understand the changes if we assume that the O-induced reconstruction of the surface leads to some form of *surface oxide*. The geometrical structure of the  $(3 \times 1)$  O surface is well understood and consists of Ni–O rows oriented along the  $[001]$  direction on top of an almost unperturbed Ni(110) substrate. Using a one-electron picture Besenbacher and Norskov [1] showed that the driving force of the reconstruction is the shift of Ni 3d levels towards the Fermi level for the Ni atoms constituting the rows which have

very low coordination. These Ni atoms can form very strong bonds with the adsorbed O atoms effectively causing the lower total energy configuration of the reconstructed surface. Scanning tunnelling microscopy showed evidence for that by demonstrating that the Ni–O rows can be moved across the surface at subsaturation coverage without this causing them to break [1].

In the one-electron picture the shift of the 3d states towards the Fermi level results in a lower electron occupation. In our multiconfigurational ground-state model this is reflected in a shift of the maximum weight from  $d^9$  towards the  $d^8$  configuration in the Ni–O overlayer. As explained in our simple picture this results in a shift of the  $d^7$  final states towards the Fermi level resulting in a smaller energy separation between  $d^7$  and  $d^8$  final states with the effect that stronger mixing occurs. For a detailed understanding of the Ni–O electronic structure we have to await further computational investigations. However, the additional feature in the  $B^2$ -spectrum clearly establishes long-range ferromagnetic order in the reconstructed layer. This indicates that exchange coupling between the Ni substrate and Ni–O overlayer dominates and is responsible for a magnetically *alive* Ni(110)–(3 × 1) O surface.

In conclusion, we have provided evidence that the resonant photoemission core-hole decay following Ni 2p x-ray absorption consists of a monopole and a quadrupole contribution. The separation of the two is facilitated by the strong difference in lineshapes of the final-state  $LS$ -multiplet structures. We further showed that the quadrupole spectrum can be used to identify the different final-state  $d^n$  configurations in Ni and so separate substrate and overlayer signals on the Ni(110)–(3 × 1) O surface. The observation of a distinctive extra quadrupole feature in the presence of oxygen provides the first unambiguous proof of long-range ferromagnetic ordering in the Ni–O overlayer.

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