Surface State Contribution to the Magnetic Moment of Ni(111)

M. Donath, F. Passek, and V. Dose

Max-Planck-Institut für Plasmaphysik, EURATOM Association, W-8046 Garching bei München, Germany

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Spin-resolved inverse photoemission measurements on Ni(111) reveal a crystal-induced surface state close to the Fermi level that is partly occupied around the $\bar{\Gamma}$ point of the surface Brillouin zone. This finding together with an observed splitting of about 100 meV between spin-up and spin-down states identifies this state as a truly magnetic state contributing to the surface magnetic moment of Ni(111). A photon polarization analysis shows that the state has Λ_1 symmetry at $\bar{\Gamma}$, therefore being derived from the p-like $L_{2'}$ bulk state.

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The ferromagnetic properties of the transition metals Fe, Co, and Ni are based on an imbalance between the number of spin-up and spin-down electrons. This is reflected in the electronic structure by a splitting of their energy bands, which results in more spin-up (majority) than spin-down (minority) occupied states. In Ni, for example, this gives rise to a net magnetic moment per atom of $0.6\mu_B$. Consequently, the partly occupied, hence truly magnetic, bands are of particular interest for studying ferromagnetism on a microscopic level. The same is true of the study of surface magnetic properties, which may be different from those in the bulk. Most calculations expect the surface magnetic moment to be enhanced by a few percent compared with the bulk magnetic moment [1].

Crystal-induced surface states usually appear in energy or symmetry gaps of the projected bulk band structure and are derived from bulk states that form the gap boundaries [2]. The wave functions of these surface states are peaked within the topmost atomic layer. Therefore, their magnetic exchange splitting $\Delta E_{\rm ex}$ contains important information on surface magnetic properties. Ordinary photoemission experiments have detected surface states just below the Fermi energy E_F on Ni(111) [3] and Ni(001) [4], leaving the spin character undetermined. An occupied surface state on Ni(110) was observed as a double-peak structure and interpreted as spin-split majority and minority spin states [5]. The first spin-resolved measurements on exchange-split surface states, occupied or empty, were performed with inverse photoemission (IPE) on Ni(110) [6] and Ni(001) [7], where totally empty surface states exhibit spin splittings $\Delta E_{\rm ex}$ comparable to the splitting of the corresponding bulk states. Besides that, an image-potential surface state on Ni(111) was found to be exchange split [8]. All these results have ruled out the existence of magnetically "dead" surface layers on the low-Miller-index surfaces of Ni. To date, however, no spin-resolved investigation has been reported that dealt with the exchange splitting of a truly magnetic surface state. In this paper, we present spin-resolved IPE measurements of a partly occupied surface state on Ni(111) which directly contributes to the surface magnetic moment.

The electronic structure at (111) surfaces of face-centered-cubic (fcc) crystals exhibits an sp-band gap extending from $L_{2'}$ to L_1. Crystal-induced surface states form at the bottom of the gap and, depending on the material, they are either occupied (Cu,Ag,Au) [9] or empty (Pd) [10] at the center of the surface Brillouin zone $\bar{\Gamma}$. With increasing $\mathbf{k}_\parallel$, they disperse to higher energy and, in the event of overlap with bulk bands of the same symmetry, they become surface resonances [11]. For Ni the situation is not as clear. The $L_{2'}$-L_1 gap ($-0.9 \rightarrow +6.0$ eV) is transversed by the uppermost d band ($L_{3\uparrow}$: -0.15 eV; $L_{3\downarrow}$: $+0.16$ eV) [3]. An sp-like surface state of Λ_1 symmetry at $\bar{\Gamma}$ was found at -0.25 eV below E_F between $L_{2'}$ and L_3. It disperses downwards in energy for $\mathbf{k}_\parallel \rightarrow \bar{K}$ [3]. An unoccupied surface state was theoretically predicted [12], but not observed in first IPE experiments on Ni(111) [13]. Later, however, an empty surface resonance was detected dispersing upwards in energy for $\mathbf{k}_\parallel \rightarrow \bar{M},\bar{M}'$ [14]. From the spin-averaged measurements at $\bar{\Gamma}$, it could not be decided whether the emission close to E_F is due to transitions into minority d states and/or into a surface state. From a theoretical point of view, the number of surface states that may exist at $\bar{\Gamma}$ for a general shape of the surface potential barrier at an fcc (111) surface is not known [15]. If there are two surface states, then both are expected to have Λ_1 symmetry. For a rectangular surface potential the calculations predict only one (occupied) surface state at $\bar{\Gamma}$, while for finite $\mathbf{k}_\parallel$ two surface states coexist. Obviously, this problem is waiting for a spin-resolved inverse photoemission experiment capable of distinguishing between minority-d-band and surface state emission.

The experimental setup for spin-resolved inverse photoemission and details about the measurement are described elsewhere [6,16]. Briefly, spin-polarized electrons are emitted by photoeffect from GaAs irradiated by circularly polarized laser light. A beam of transversely polarized electrons impinges on the Ni(111) surface with a divergence of less than 2°. The angle of electron incidence Θ with respect to the surface normal is experimentally defined with an accuracy of better than 2°. The azimuth chosen for the present study is the $[\bar{1}10]$ direction, which corresponds to $\bar{\Gamma}\bar{K}$ of the surface Brillouin zone. Spectra measured for positive and negative Θ in this azimuth are equivalent with respect to the incoming electron beam. The photon emission intensities, however, may be different due to the nonequivalent photon detection geometry. The sample is a single crystal cut into a hexagonal picture frame shape with its sides oriented along ⟨110⟩ directions and the [111] direction perpendicular to the hexagon plane. The magnetic state of the sample was monitored by Kerr microscopy. A high-current pulse through a magnetization coil wound around one leg of the sample leads to a single-domain remanent magnetization. The surface was prepared by sputtering with 1.2 keV argon ions and subsequent annealing at 950 K. Low-energy electron diffraction and Auger electron spectroscopy were used to characterize the sample. Photons emitted from the sample are detected in energy-selective Geiger-Müller counters with a detection energy of 9.4 eV. The overall apparatus function is described fairly well by a Gaussian function with FWHM of 450 meV. All IPE data presented here are recorded at room temperature, where the magnetization is only slightly reduced compared with the ground state.

IPE data of Ni surfaces always exhibit a peak just above E_F, usually interpreted as a result of direct and/or indirect transitions into the uppermost minority d band with its high density of states [13,14]. This interpretation is supported by spin-resolved measurements clearly demonstrating the almost pure minority character of emission features close to E_F [6,7,17]. An example thereof is displayed in Fig. 1(a), showing a direct transition into a minority d state observed on Ni(110) [6]. Our data for normal electron incidence on Ni(111) displayed in Fig. 1(b) reveal a very different situation. While the spin-integrated emission intensity close to E_F looks almost the same as in Fig. 1(a), the spin-resolved data exhibit considerably smaller spin asymmetry $A=(I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)$. Since at $T=0$ no empty majority d states are available in Ni, we conclude that at least the observed spin-up emission from Ni(111) at E_F does not originate from transitions into d states.

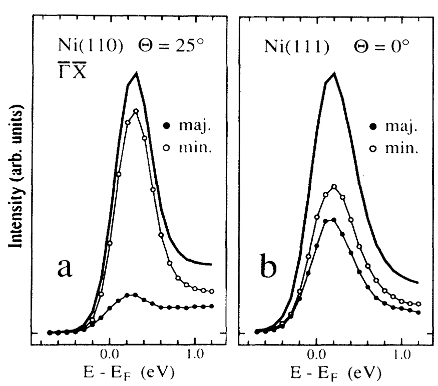

FIG. 1. Spin-integrated (solid lines) and spin-resolved (open and closed circles) inverse photoemission spectra of Ni(110) (a) and Ni(111) (b) in the vicinity of the Fermi energy E_F. Spin resolution reveals the considerably different origin of the otherwise similar emission features.

One might suggest that the emission is due to transitions between sp-like bands with their smaller exchange splitting compared with d states. We have tested this hypothesis by angle-resolved measurements in the $\bar{\Gamma}\bar{K}$ azimuth. Our results are summarized in the $E(\mathbf{k}_\parallel)$ plot of Fig. 2. The nonhatched areas define an energy gap of the projected bulk band structure confined by a solid (dashed) line for the majority (minority) spin system. S' (open circles) denotes the occupied surface state measured by photoemission [3]. Indirect transitions into empty minority d states appearing with small intensity independent of $\mathbf{k}_\parallel$ are not included in the diagram. Apart from them, two prominent features are observed above E_F: S and B. With increasing $\mathbf{k}_\parallel$, S disperses upwards in energy while losing intensity and broadening the more it overlaps with bulk states. For finite $\mathbf{k}_\parallel$, S represents the already observed surface resonance [14]. For $k_\parallel \geq 0.15$ Å^{-1}, feature B crosses E_F from below, first for spin-down (open triangles), and then at larger $k_\parallel$ also for spin-up electrons (closed triangles). Comparing the dispersion of B with calculations within a combined interpolation scheme (dashed and solid lines in Fig. 2), we identify B as due to transitions between sp-like bulk bands. Note that for $\mathbf{k}_\parallel$ around $\bar{\Gamma}$ this transition is clearly below E_F and does not contribute to the IPE intensity. As a consequence, the observed strong emission close to E_F around $\bar{\Gamma}$ does not originate from transitions between sp-like states either.

To clarify the origin of feature S in the vicinity of $\bar{\Gamma}$, we tested its sensitivity to surface contamination. Spectra for clean and contaminated Ni(111), i.e., exposed to 0.9 L of CO (1 L$=10^{-6}$ torr sec), are shown in Fig. 3(a). The spectra have been normalized to equal background intensity. The remaining feature close to E_F on the contaminated surface exhibits high spin asymmetry interpreted as indirect transitions into minority d states, which

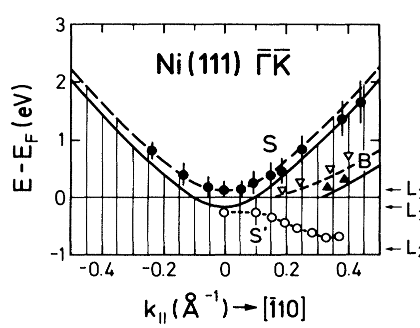

FIG. 2. $E(k_\parallel)$ diagram for Ni(111) in the $\bar{\Gamma}\bar{K}$ azimuth: occupied surface state S' (open circles) [3], empty surface state/resonance S (closed circles, spin integrated), and bulk sp-band transition B (triangles, spin resolved).

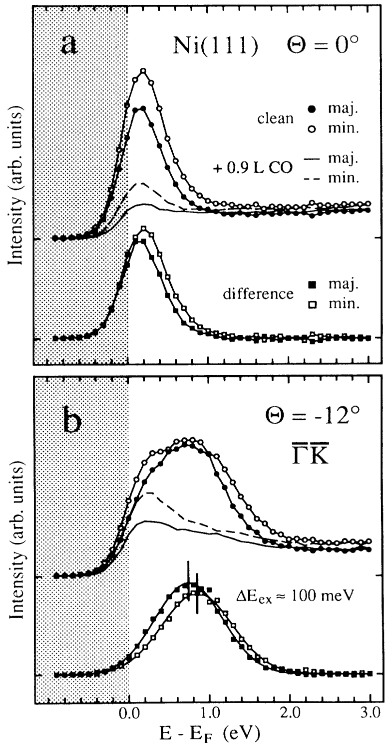

FIG. 3. Spin-resolved IPE spectra of Ni(111) for normal electron incidence (a) and $\Theta = -12°$ (b): clean surface (open and closed circles), surface exposed to 0.9 L of CO (dashed and solid lines), and difference spectra (open and closed squares).

are known to be not very surface sensitive [6]. The spin-resolved difference spectra, also shown in Fig. 3(a), reveal a surface-sensitive feature with spin-split high-energy, but identical low-energy flank. This result provides evidence of the interpretation of S as an exchange-split surface state which is cut off by the Fermi function at least for the majority part and therefore only partly empty/occupied. To deduce the exchange splitting of S, we made measurements for $\Theta = -12°$, where it appears completely above E_F for both spin directions. The photon detection angle was chosen such that the spectra are not influenced by transition B due to photon polarization effects. In Fig. 3(b) spectra taken at $\Theta = -12°$ for clean and contaminated Ni(111) are shown with their difference. The difference spectra exhibit S well separated from the background and d-state intensities. Fitting them with Gaussians [solid lines through the data points in Fig. 3(b)] determines the peak positions to be $E - E_F = 0.744 \pm 0.015$ and 0.850 ± 0.015 eV for majority and minority electrons, respectively. This results in a magnetic exchange splitting of 106 ± 22 meV (for $\Theta = -12°$).

Analyzing the angular distribution of the emitted photons to characterize the symmetry of S shows increasing photon intensity with increasing photon takeoff angle relative to the surface normal. The observed z polarization proves S to have Λ_1 symmetry. Consequently, it is derived from the p-like $L_{2'}$ point rather than the d-like L_3 point. It is a true surface state in a symmetry gap at $\bar{\Gamma}$. With increasing $\mathbf{k}_\parallel$ and therefore reduced symmetry, S develops into a surface resonance overlapping with bulk states of the same symmetry.

In conclusion, the high intensity observed in IPE spectra for normal electron incidence on Ni(111) has been attributed predominantly to a partly occupied spin-split surface state. Contributions from direct transitions into empty minority d states or between sp bands have been ruled out for a photon energy of 9.4 eV. Indirect transitions into minority d states have been separated from the surface state emission by adsorption experiments and are shown to play only a minor role. The present angular-resolved experiment gives strong evidence that S does exist, not only for finite $\mathbf{k}_\parallel$, but also at $\bar{\Gamma}$. There, the partly empty surface state S has Λ_1 symmetry and is derived from the bottom of the sp-band gap $L_{2'}$-L_1 as its occupied counterpart S'. The observed magnetic exchange splitting of about 100 meV has the same size as the splitting of the p-like gap boundary $L_{2'}$ [18]. Exchange splitting and partial occupation define this state as a truly magnetic surface state which actually contributes to the magnetic moment of the Ni (111) surface. Since the experiment gives information on specific points in $\mathbf{k}$ space rather than averaging over the whole Brillouin zone, no quantitative conclusion about a possibly enhanced surface magnetic moment can be drawn. Nevertheless, electronic states of this kind, located at the crystal/vacuum interface, partly occupied, and spin split, are an extremely sensitive tool for the study of magnetic properties at surfaces and interfaces. In particular, they are a sensor of changes of the exchange coupling caused by adsorption or deposition of another material.

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