Observation of an exchange-split alloy surface state

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The spin-resolved electronic structure at the (110) surface of the magnetic alloy FeNi₃ has been studied with spin-polarized inverse photoemission spectroscopy in conjunction with first-principles electronic structure calculations. An unoccupied \overline{Y} Schockley surface state in a bulk band gap is observed that is exchange split by 320 meV, indicating that the topmost surface layer is ferromagnetically ordered.

Multicomponent magnetic systems and layered structures are rapidly gaining importance as materials with properties tailored to a number of specific applications. Fe_xNi_{1-x} alloys are an important example, the phase diagram containing a variety of structural, mechanical, and magnetic properties. These include the Kondo effect¹ and the Invar phenomenon.² Of particular fundamental interest is the complexity of the interaction between the magnetic and chemical ordering in these materials. Theoretical studies have suggested^{3,4} that magnetic anomalies arise from an antiferromagnetic coupling between nearest-neighbor iron atoms. Furthermore, the chemical and magnetic ordering have been shown to have a large influence on each other in the region of the orderdisorder transitions.^{5,6}

Technologically important nickel-iron alloys usually have compositions around 75–82% Ni. They are referred to as *Permalloys* due to their high permeabilities and low coercivities. There have been a limited number of investigations of the electronic structure of FeNi₃ (Refs. 7 and 8) and the results have been interpreted using the band structure of nickel.⁸ Spin-resolved soft x-ray appearance potential spectra of FeNi₃ (Ref. 9) have shown how Fe, a "weak" ferromagnet as a pure element, becomes a "strong" ferromagnet in the compound accompanied by an increased magnetic moment of about $3\mu_B$. Ni, on the other hand, was observed to become more "Fe-like."

An understanding of the magnetic behavior of Fe-Ni alloys requires detailed knowledge of the electronic structure, since the latter plays a key role in determining the magnetic properties. For example, Permalloys have recently been widely employed in magnetoresistive sensor devices such as spin valves and tunnel junctions. In the latter application it has been shown that the junction magnetoresistance is strongly dependent on the surface magnetization as well as the electronic density of states.¹⁰ In order to further understand these key properties we have employed spin-polarized inverse photoemission measurements and first-principles electronic structure calculations of $FeNi_3(110)$ to investigate the surface magnetism and the spin-resolved electronic structure. Information on the surface magnetic properties can be retrieved via the exchange splitting of crystal-induced surface states, which usually appear in energy or symmetry gaps of the projected bulk band structure and are derived from the bulk states that form the gap boundaries.¹¹ Our results demonstrate the existence of an exchange-split alloy surface state.

Experiments were carried out using a picture-frameshaped FeNi₃(110) single crystal with legs in the $\langle 111 \rangle$ directions of easy magnetization. Before insertion into vacuum, the mechanically polished crystal surface was electrochemically etched in a 9:1 mixture of 85% H₃PO₄ and CrO₃. Once in UHV, repeated cycles of Ar⁺ sputtering (1 kV, 10 min) and annealing (973 K, 25 min) were employed to obtain a depletion of sulfur and carbon in the surface layer. Subsequent Auger spectra corresponded to a clean stoichiometric surface and a sharp 1×1 low energy electron diffraction pattern was observed.

Magneto-optic Kerr effect (MOKE) measurements were carried out *in situ* to evaluate the field necessary to achieve saturated magnetization and to determine whether the sample could be magnetized in remanence.¹² The magnetic field was generated by passing a current through a coil of tantalum wire wound around one leg of the picture frame crystal. The measurements were performed by ramping the current through the coil while monitoring the rotation of linearly polarized light admitted through a vacuum window, reflected at the FeNi₃(110) surface, and analyzed through another window.

The angle-resolved spin-polarized inverse photoemission spectroscopy (SPIPES) measurements employed a GaAs spin-polarized electron source¹³ to supply a well-defined beam of spin-polarized electrons to the FeNi₃(110) sample. The angle between the magnetization direction [111] and the spin vector direction of the electrons, which was aligned with the $[1\overline{1}0]$ direction in the surface plane, was constant at 35.3°. The polar angle of incidence with respect to the surface normal, θ , could be varied with the parallel component of the electron wave vector \mathbf{k}_{\parallel} lying along the |001| direction. To ensure that the sample magnetization remained saturated, all the measurements were recorded with a small current being passed through the magnetizing coil. This generated a field sufficiently strong to keep the magnetization saturated, while still weak enough not to have any observable effect on the position of the electron beam.

Photons were counted using two solid-state photon detectors.¹⁴ Both were fitted with a SrF_2 window low-pass

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filter and a NaCl photocathode high-pass filter, giving an optical resolution of 0.42 eV,15 which dominates the overall experimental resolution. The effective energy of the detected photons is \sim 9.5 eV. The photon detectors were mounted at angles of 41° and 71° with respect to the electron beam direction. The two spin channels were measured quasisimultaneously by flipping the electron spin direction, while keeping all the other parameters constant for each data point. Photons were counted during a time interval corresponding to a constant accumulated charge of incident electrons of 2 μ As at the sample. The electron source cathode was operated under nonoptimized negative electron affinity conditions,¹³ leading to a constant emission current for several hours. Several spectra were added channelwise to obtain acceptable statistics. The spin-resolved data were renormalized for a 100% polarized electron beam.^{13,15}

The FeNi₃(110) sample proved to be extremely sensitive to contamination, resulting in the complete attenuation of clean-surface features in the SPIPE spectra within about an hour of scanning, despite a base pressure below 2 $\times 10^{-10}$ mbar. The Auger spectra recorded subsequently showed a significant amount of carbon contamination. Since this was insufficient time to obtain acceptable statistics it became necessary to remove this contamination from the surface with repeated sputter and anneal cycles before any additional spectra could be recorded. This process was repeated several times in order to gain satisfactory statistics.

First-principles electronic structure calculations were performed for both the bulk FeNi_3 alloy and the $\text{FeNi}_3(110)$ surface. These electronic structure calculations were based on the well-known density-functional theory¹⁶ with the usual local-density approximation.¹⁷ Random substitution disorder was approximately described by the so-called virtual crystal approximation.¹⁸ The FeNi₃(110) surface was modeled by a slab-supercell approach. The supercell consisted of a slab of 15 FeNi₃ atomic layers and a slab of vacuum 7 atomic layers thick. In many previous calculations of other systems, the surface was modeled by a slab of 5–7 atomic layers. Here we found that a slab of more than 11 atomic layers is necessary to achieve convergence of surface states. The ideal fcc structure was assumed for the virtual crystal. We used the well-known linear muffin-tin orbital method.¹⁹

The in situ MOKE hysteresis loops as a function of temperature are described elsewhere.¹² Prior to heating the sample, the hysteresis loops were curved, with strongly reduced remanence magnetization with respect to the saturation value. The loops recorded after field cooling from above the Curie temperature of about 855 K adopt a square appearance with a smaller saturation field as well as a lower coercivity and saturation in remanence. Further hysteresis loops measured at room temperature after this process showed a retention of the square appearance, indicating that the heating process changes the magnetic properties of the sample irreversibly via the presence of an induced uniaxial anisotropy.²⁰ Further MOKE measurements showed that once magnetized, the remanent magnetization decayed from the saturation value, probably due to external stray fields exceeding the very small coercivity. Hence the constant application of a small field was required to keep the sample magnetization saturated.



FIG. 1. (a) SPIPE spectra of room-temperature $\text{FeNi}_3(110)$ recorded with an electron incidence angle of 30° in the [001] azimuth. Photons at an energy of 9.5 eV were counted in both detectors. Open (closed) circles refer to data recorded with minority-(majority-) spin electrons. The lines between points represent the fitted function and the vertical lines indicate the peak positions determined by the fitting procedure. (b) Spin averaged spectra from the photon detectors at 11° (closed squares) and 41° (open squares) with respect to the sample surface normal.

Figure 1(a) shows FeNi₃(110) SPIPE spectra recorded at an electron incidence angle of 30° following field cooling through the Curie temperature. The peak positions that are indicated by vertical lines in Fig. 1(a) were determined by fitting a function to each spectrum. Each peak was represented by a Gaussian and the background by a linear function multiplied by the integrated photon detector response function to account for the step representing the onset of available unoccupied states at the Fermi level. As expected, the peaks in the minority-spin spectrum consistently occur at higher energy than the corresponding majority-spin features.

The feature C seen at ~ 2.5 eV above E_F in Fig. 1(a) is interpreted as a surface state on the basis of several observations. First, it attenuates rapidly with exposure to residual gases in the UHV chamber. Such attenuation is characteristic of a surface state.²¹ Second, as can be seen in the spectra in Fig. 1(b), feature C is not observed in the data from the photon detector that is at an angle of 41° with respect to the electron beam, and hence at an angle of 11° with respect to the surface normal. This suggests that the transition dipole for feature C is mainly perpendicular to the surface.²² This is also behavior typical of a surface state. Third, as illustrated by Fig. 2, feature C follows an energy vs \mathbf{k}_{\parallel} dispersion very similar to that observed for the Ni(110) Schockley surface state in the \overline{Y} azimuth.^{15,21,23} The latter occurs in a projected bulk band gap at about the same energy as feature C. Moreover, first-principles electronic structure calculations for bulk FeNi₃ alloy exhibit a projected bulk band structure where a band gap exists around \overline{Y} at the energy of feature C. Finally, first-principles electronic structure calculations of the FeNi₃(110) surface exhibit surface bands along ΓY that reproduce the dispersion of feature C apart from a shift of



FIG. 2. Energy vs parallel momentum diagram of the projected bulk band structure (shaded) of $\text{FeNi}_3(110)$. The shaded area represents projected bulk bands. Full and dashed lines represent calculated majority-spin and minority-spin surface bands, respectively. Closed and open circles represent majority-spin and minority-spin experimental peak positions, respectively. The dispersion of the features *A*, *B*, and *C* in Fig. 1(a) can readily be seen.

about 0.5 eV and are mainly centered on the surface layer with a 30% (20% of p_z and 10% of *s* orbitals) contribution from the topmost atomic layer. The calculated projected bulk band structure and surface bands are shown in an energy vs parallel momentum $E(\mathbf{k}_{\parallel})$ diagram in Fig. 2 along with the positions of experimentally observed peaks.

The similarity beween our inverse photoemission results for FeNi₃(110) here and Ni(110) (Ref. 15) is consistent with previous FeNi₃ photoemission results.⁸ Indeed, the latter were explained by reference to the band structure of pure nickel. This was possible since the electronic spectral density in compositionally disordered fcc alloys can be classified using the same symmetries as in pure Ni and the same polarization-dependent selection rules apply. By comparison to results from clean Ni,^{15,21} the observed spectral features observed here for FeNi₃ can be explained as follows. The first peak *A* seen only in the minority spin channel arises from transitions into empty 3*d* bands. The next feature *B*, which occurs in both spin directions, was assigned in the case of Ni(110) to transitions into states of a mainly *s*-*p* character, although with a significant hybridization with 3*d* bands.¹⁵ As noted above, the surface feature about 2.5 eV above the Fermi level in both spin directions *C* occurs in an inverted Shockley gap of the Ni bulk band structure.

Finally, we consider the experimental exchange splitting of SPIPE features. A comparison with the analogous Ni(110) features¹⁵ indicates that the splitting for FeNi₃(110) is almost a factor of 2 larger. The FeNi₃(110) s-p-like feature is split by about 550 meV compared to about 300 meV for Ni(110), while the $FeNi_3(110)$ surface state splitting of about 320 meV compares with 190 meV for Ni(110). The larger spin splitting can be understood if one considers that a Ni crystal, with its magnetic moment of $0.6\mu_B$ per atom is being diluted with 25% Fe (magnetic moment $2.1\mu_B$) leading to the FeNi₃ moment of $1.15\mu_B$. The increased spin splitting approximately follows the increase in magnetic moment. The magnitude of the observed surface state exchange splitting is hence consistent with a bulk-terminated surface. The existence of this exchange splitting indicates that the topmost FeNi₂(110) surface layer is ferromagnetically ordered. Finally, the sign of the splitting demonstrates a ferromagnetic coupling between the surface layer and the bulk at room temperature.

In summary, we have investigated the spin-resolved electronic structure of FeNi₃(110). Inverse photoemission data and theoretical calculations point to the existence of a surface state at \overline{Y} on the alloy surface. This surface state exhibits an exchange splitting of about 320 meV, which demonstrates the ferromagnetic nature of the alloy surface layer and its coupling to the bulk.

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