Magnetic Exchange Splitting of Electronic Surface States on Ni(110)

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The temperature-dependent magnetic exchange splitting of an electronic surface state located at the $\bar{S}$ point of the Ni(110) surface Brillouin zone has been measured. The measured value of the splitting is 0.30 ± 0.02 eV at 100 K which is equal to the exchange splitting of the bulk bands of Ni (0.31 ± 0.04 eV) from which this surface state is derived. This result directly rules out the existence of a paramagnetic or magnetically "dead" surface layer on Ni(110).

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The magnetic properties near a surface can be quite different from the corresponding bulk properties. There are only a few measurements on the magnetic properties of single-crystal surfaces of ferromagnetic metals (primarily Ni), and the results are contradictory. The spin polarization of the photoyield of electrons emitted from Ni(100) shows a reversal of sign approximately 0.1 eV above threshold.[1] These measurements have been quantitatively explained in terms of a band-structure photoemission calculation with the exchange splitting as a parameter.[2] The magnitude of the required exchange splitting was 0.33 eV, which is in excellent agreement with the measured bulk value of 0.31 eV.[3] The calculations showed that the experimental result was very insensitive to the surface magnetization, i.e., a "dead layer" would have only a marginal effect.[2] Spin-polarized field-emission measurements on Ni(100) have been interpreted as showing that the surface and bulk magnetic properties are very similar.[4] On the other hand, the temperature dependence of the magnetization at a Ni(110) surface has been measured by polarized low-energy electron diffraction, showing significant differences from bulk Ni.[5] The fact that none of these experiments was capable of measuring the surface exchange splitting or magnetic moment still leaves open the possibility that single crystals of Ni have a magnetic "nearly dead" layer. These dead layers have been seen in thin Ni films on nonmagnetic metallic substrates.[6]

This Letter reports the observation of an exchange-split surface state at the corner of the surface Brillouin zone of Ni(110) with angle-resolved photoelectron spectroscopy. The experimentally observed splitting of the surface state compared to the measured bulk exchange splitting[7] in the bands from which the states are derived gives directly (within the context of a simple model) the local magnetic moment at the surface compared to the bulk value. The measurements were made with an angle-resolved photoelectron spectrometer at the Synchrotron Radiation Center of the University of Wisconsin. The system resolution was 150 meV.

Figure 1 shows two photoemission spectra taken at a photon energy of 34 eV and a collection angle corresponding to the $\bar{S}$ point in the surface Brillouin zone. These spectra show that there are two peaks in the clean spectrum which are very sensitive to the adsorption of CO. Figure 2 shows the relationship of the bulk and surface Brillouin zones and the line in the bulk zone that projects onto $\bar{S}$ in the surface zone. These lines run from W to L to W in the bulk, i.e., along Q symmetry lines. We will show that the two peaks observed in the spectra shown in Fig. 1 are surface states and that the temperature-dependent data prove that they are exchange-split surface states. A peak in a photoemission spectrum must fulfill several criteria before it can be classified as a surface state. Such a state has to be two-dimensional; no dispersion with momentum normal to the surface should be observed. This

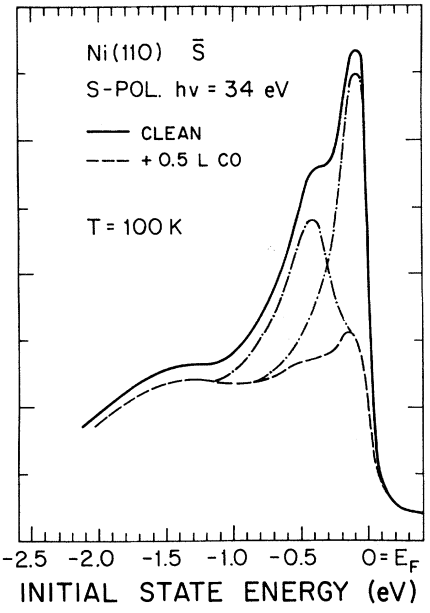

FIG. 1. Photoemission spectra showing the effects of CO adsorption (1 L=10^{-6} Torr sec). Dot-dashed curves are fits to the two surface-state peaks.

state should fit into a gap of the appropriate symmetry of the projected bulk band structure. Furthermore, surface states in general are sensitive to contamination.

Figure 1 already presented evidence for the surface sensitivity of the two peaks in the spectrum. The two states are almost totally quenched by exposure to 0.5 L of CO at 100 K. The same intensity decrease was observed after adsorption of N_2 and O_2, but not after H_2 adsorption at 100 K. The two-dimensionality of the peaks shown in Fig. 1 was confirmed by measuring spectra as a function of photon energy, keeping the value of $k_{\parallel}$ (parallel component of momentum) fixed at the $\bar{S}$ point in the surface zone. There was no observed shift in the initial-state energy of either of these states when the photon energy was changed from ~20 to ~50 eV. If we assume free-electron final states in the bulk then this range of photon energy corresponds to sweeping the perpendicular component of the momentum over 80% of the distance from L to W in Fig. 2.

The final step is to show that the states lie in band gaps in the projected bulk band structure. Figure 3 shows the measured band structure along the Q line from L to W.[8] There are two different symmetry bands in the Q direction. These are labeled Q_1 and Q_2. Q_1 bands contain functions like x^2, y^2, z^2, or xy (z normal to the surface) and Q_2 bands contain functions like xz or yz. The band structure shown on the left of Fig. 3 can be used to project the bulk band structure along Q onto the point $\bar{S}$ in the surface Brillouin zone (shown at right). We find a gap in the Q_2 bands extending from E_F to ~ – 0.5 eV for the minority bands and from ~ –0.2 to –0.8 eV for the majority bands. The observed surface states

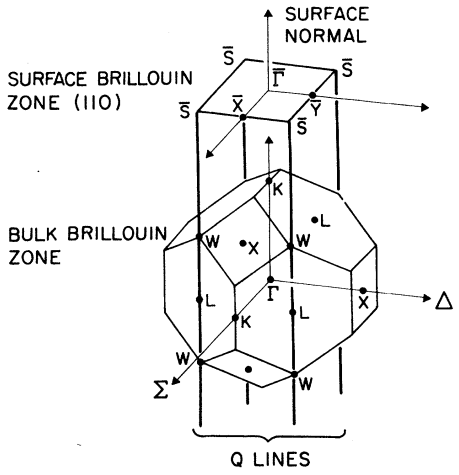

FIG. 2. Projection of the bulk Brillouin zone onto the (110) surface Brillouin zone.

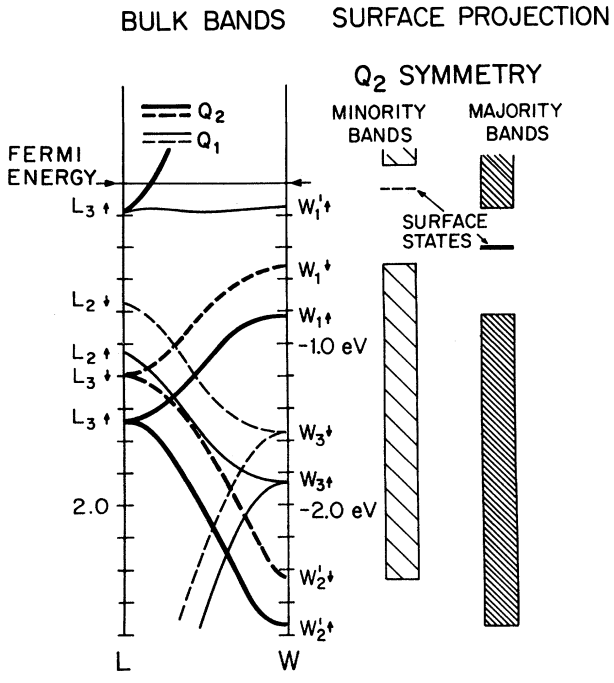

FIG. 3. Band structure of Ni along the Q line from L to W. The surface projection of the minority and majority Q_2 symmetry bands is shown at the right.

fit very nicely into these gaps. In the excitation geometry chosen, for s polarization of the incoming light, only initial states of Q_2 symmetry can be excited. These selection rules are given elsewhere.[9]

The arguments presented above prove that we are observing two surface states. Figure 4 shows the temperature dependence of the splitting between these two states. As the temperature is raised the two peaks coalesce, which is what a long-range-order model of the magnetization would predict.[3] The splitting between the minority- and majority-band surface states at 100 K was determined by computer fitting the spectra with two Gaussian curves of equal area (see Fig. 1). The width of a peak increases as the energy separation from the Fermi energy increases because of the increased Auger lifetime broadening.[10] This fit, which is shown in Fig. 1, gave a splitting of 0.30 ± 0.02 eV at 100 K, with the two peaks being at -0.11 and -0.41 eV. Therefore, the exchange splitting of the surface state (0.30 ± 0.02 eV) is equal to the measured bulk exchange splitting (0.31 ± 0.04 eV).[7]

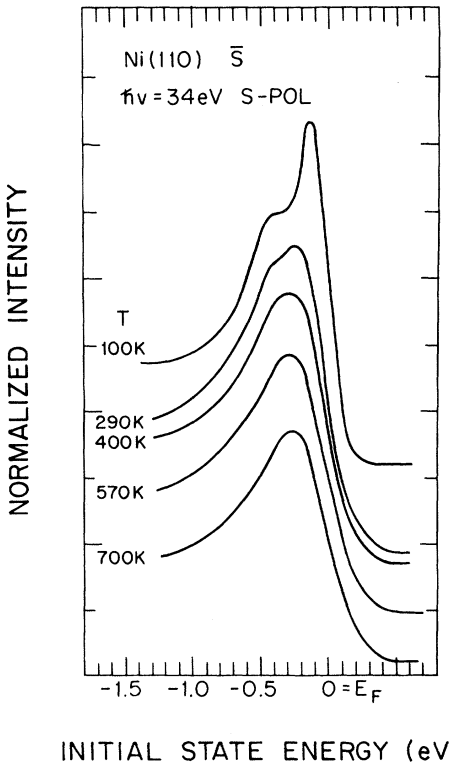

FIG. 4. Temperature dependence of the spectra taken at 34-eV photon energy.

There are three different interpretations of the temperature-dependent spectra shown in Fig. 4. Each interpretation leads to a different temperature dependence of the exchange splitting and consequently a different picture of the local magnetization near the surface. The first procedure is to fit all of the spectra with two peaks whose width is given by the low-temperature data. This fitting procedure yields an exchange splitting of ~0.15 eV at 700 K, above the Curie temperature ($T_C = 651$ K). The temperature dependence of the splitting is similar to that reported by Eastman, Himpsel, and Knapp[3] for the bulk bands of Ni. The exchange splitting persists above T_C, which implies that short-range magnetic order exists above T_C.[12]

The second interpretation of the temperature dependence of the spectra is due to a model proposed by Korenman and Prange.[12] Their theoretical analysis predicts that the local magnetization, which is proportional to the splitting seen in the photoemission experiment, is nearly temperature independent. They were able to analyze the temperature dependence of the bulk spectra[3] with a nearly constant exchange splitting. The physical explanation is that photoemission is accompanied by emission and/or adsorption of an arbitrary number of magnons. At low temperatures this would produce well-defined magnon satellites, but near T_C the magnons are so numerous and couple so strongly that the line shape is "renormalized." The inherent width of the peaks in the spectra due to Auger decay makes it impossible to resolve magnon satellites at low temperature.

There is a third way to analyze the data which leads to a linear decrease in the exchange splitting with increasing temperature, reaching zero at the Curie temperature. We were forced to conclude that the exchange splitting persisted above T_C because the peak at high temperature in Fig. 4 was too wide to be fitted with two degenerate peaks with a width given by the low-temperature data.[11] If we assume a linear dependence of the width with a temperature coefficient of $\sim 4 \times 10^{-4}$ eV/K the exchange splitting at 700 K is zero. There are no measurements of the temperature dependence of surface states near the Fermi energy of Ni. The magnitude of the temperature dependence of the d band peaks in Cu is reported to be $\sim \frac{1}{2}$ of the required number.[13] This fact led Eastman, Himpsel, and Knapp[3] to conclude that the width of the peak in the bulk spectra of Ni could not be explained by a tem-

perature-dependent width.

The first two models which predict, respectively, ~50% and ~0% reduction in the exchange splitting slightly above T_C must be resolved theoretically. The third model can be checked experimentally by careful measurements of the temperature dependence of the width of an isolated surface state on Ni close to the Fermi energy.

The measured splitting of the exchange-split surface states at low temperatures is within experimental uncertainty equal to the measured bulk splitting. We can estimate the possible deviation of the local magnetic moment at the surface compared to the bulk using our data and a simple model. The surface state is assumed to decay exponentially into the bulk and only the outer surface layer is allowed to have a different magnetic moment. If the surface state is totally localized to the first layer then the uncertainties in the surface and bulk measurements produce a ±19% possible deviation in the local magnetic moment at the surface compared to the bulk. If the exponential decay length of the surface state is (a) one, (b) two, or (c) three layers then the possible deviation grows to (a) ~22%, (b) ~30%, and (c) ~35%. Most calculations for Ni give a decay length of states near the Fermi energy of from one to three layers.[14,15]

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First-Principles Calculation of Diamagnetic Band Structure

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For a simple nontrivial model potential, the full quantum mechanics of the Bloch electrons in rational magnetic fields is reduced to a one-dimensional eigenvalue problem and the exact diamagnetic band structure is calculated from first principles. Agreements with and deviations from the predictions of the semiclassical Onsager dynamics are found and discussed.

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In spite of considerable efforts[1,2] a first-principles justification for the so-called semiclassical method for Bloch electrons in a magnetic field, i.e., for the use of the effective Hamiltonian

$$H_{\text{eff}}=E_n(\vec{p}/\hbar-e\vec{A}/\hbar c) \tag{1}$$