RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 31, NUMBER 10 15 MAY 1985

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Electronic properties of $p(1\times1)$ Ni films on Cu(100)

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(Received 11 February 1985)

Angle-resolved photoelectron spectroscopy is used to determine the electronic structure and magnetic exchange splitting of an ordered nickel monolayer on Cu(100).

Recent interest in the magnetic properties of surfaces and interfaces may be attributed to several related factors.[1-3] Two primary factors have been the development of new experimental techniques, capable of providing definitive information about electronic and magnetic properties of surfaces, and the advancement of computational techniques which now yield accurate and physically meaningful results based on first-principles calculations. The highly successful use of angle-resolved photoemission spectroscopy to determine the bulk electronic properties of ferromagnetic metals[4-6] has led to corresponding experiments aimed at probing magnetic surface states at transition-metal surfaces.[7,8] The experiments have continued to verify the remarkable achievements of self-consistent calculations in providing accurate energy bands for both bulk[9,10] and surface electronic states[11-15] in transition-metal ferromagnets. More recent interest has focused on the properties of freestanding Ni films,[15-17] Ni layers[18-20] on nonmagnetic surfaces, and on interfaces incorporating various magnetic materials. The substantial success of these coordinated experimental and theoretical studies in advancing our understanding of the electronic and magnetic properties of homogeneous materials provides a strong indication that surface and interface magnetism in the layered systems can also be successfully studied.

Several recent first-principles calculations have predicted the electronic and magnetic properties of ordered Ni films on a Cu(100) surface.[18-20] These calculations address issues related to conflicting experimental results concerning magnetically inactive layers. Magnetically inactive layers have been reported to exist for less than two layers of Ni deposited on Cu based on susceptability measurements.[21] Hall-effect[22] measurements seem to confirm the existence of the inactive layers, but electron-capture spectroscopy measurements[23] and spin-polarized photoemission measurements[24] predict that even a single monolayer of Ni on Cu is not magnetically inactive. Relevant calculations[17-20] all predict a decrease in magnetic moment of a Ni monolayer on Cu(100) (it is reduced by about 40% from the theoretical bulk value) but do not predict a magnetically inactive layer. There have not been any direct experimental tests (i.e., by photoemission) of the theoretical predictions for the Ni/Cu(100) system to date, and questions pertaining to the accuracy of the calculations as well as the existence of inactive layers in the $p(1\times1)$ Ni/Cu system remain unresolved.

This paper presents the first direct measurements of the two-dimensional electronic structure and magnetic exchange splitting of a $p(1\times1)$ monolayer of Ni atoms on Cu(100). These new results show that the calculated electronic structure of the Ni/Cu(100) system is substantially correct, and that the predicted exchange splitting of 0.3 eV is correct within experimental error. The results imply (but do not prove) that there is not a magnetically inactive layer at the Ni/Cu(100) interface or for a monolayer of Ni atoms on Cu(100) in agreement with the calculations.

Our experiments were performed using synchrotron radiation from the Tantalus storage ring in Stoughton, Wisconsin. The 1-m stainless steel Seya-Namioka monochromator was used to disperse the light, and an angle-resolving photoelectron spectrometer, described previously,[6] was used to obtain photoemission spectra. Energy resolution (combined monochromator and analyzer) was better than 100 meV at all energies, as judged by the Fermi edge, and angular resolution was fixed at ±1.2°.

The Cu(100) crystal was spark cut and aligned to ±1° accuracy using standard x-ray Laue methods, and cleaned *in situ* by Ne sputtering and annealing. Crystal order was checked using low-energy electron diffraction (LEED), and surface contamination was monitored using Auger electron spectroscopy (AES). Nickel was deposited on the clean Cu surface by evaporation from a resistively heated tungsten filament. The filament electrodes and evaporation chamber were water cooled to maintain low pressures (10^{-10} Torr) during vapor deposition.

Previous experimental work[25-27] has shown that good quality epitaxial films of Ni can be grown on Cu substrates, and has established the upper temperature limit required to avoid interdiffusion at the interface ($<240\,^{\circ}\mathrm{C}$). For Ni

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overlayers in the 1–3 monolayer thickness range, the Cu *d* bands persist in the photoemission spectra along with the Ni *d* bands, and the intensity ratio of these structures for a fixed set of experimental conditions (i.e., *s*-polarized light, $\hbar\omega = 21.2$ eV, normal emission) serves as a relative thickness calibration. An absolute thickness calibration accurate to ±0.2 monolayer was obtained based on AES line intensities of Cu and Ni (as described by Tear and Roll[25]) and by independent calibrations of our quartz thickness monitor based on Dektac profilometer measurements.

Electron energy distribution curves (EDC's) were obtained for several $p(1\times1)$ Ni overlayers of thickness ranging from 1–4 monolayers. Two distinct high-symmetry configurations were used which permitted the even- and odd-symmetry two-dimensional electronic bands to be experimentally separated. EDC's taken at fixed values of $k_{\parallel}$ with different photon energies confirmed the two-dimensional nature of the Ni *d*-band features at 1–2 monolayer coverages (refer to Fig. 1). Bands along the $\overline{\Gamma}-\overline{M}$ direction, were studied with the crystal oriented so that the [11] direction was parallel to **A**, the light polarization vector. Even-symmetry bands were probed by collecting electrons in a plane parallel to the [11] axis at polar angles θ corresponding to the desired value of $k_{\parallel} = \sqrt{2mE_k/\hbar^2}\sin\nu$ where $k_{\parallel}$ is the component of electron wave vector parallel to the surface and E_k is the kinetic energy of the emitted electron. Odd-symmetry bands were probed with **A** along the [11] axis and emission angles along the $[\bar{1}1]$ axis. Corresponding even- and odd-symmetry data were obtained for the $\overline{\Gamma}-\overline{X}$ direction by orienting the [01] direction along **A**.

Figure 1 displays a typical set of EDC's for odd-symmetry initial states along the $\overline{\Gamma}-\overline{M}$ direction corresponding to $k_{\parallel}$ values extending to the zone edge. A complete set of data for even- and odd-symmetry states along $\overline{\Gamma}-\overline{M}$ and $\overline{\Gamma}-\overline{X}$ was obtained for several photon energies and for $p(1\times1)$ films having thicknesses ranging from one monolayer to over three monolayers. Figure 2 summarizes the results for one-monolayer data by plotting the binding energy of peaks in the EDC's vs $k_{\parallel}$. Some two-monolayer data are also presented. This figure constitutes a fairly rigorous test of the slab calculations for a $p(1\times1)$ Ni monolayer on Cu(100). It is clear that the calculations[18–20] are in substantial agreement with our experimental results.

The slab calculations[18–20] predict an exchange splitting of a $p(1\times1)$ Ni monolayer on Cu(100) of approximately 0.3 eV. Our energy resolution (100 meV) was sufficient to resolve the exchange splitting of the Ni monolayer at a few selected

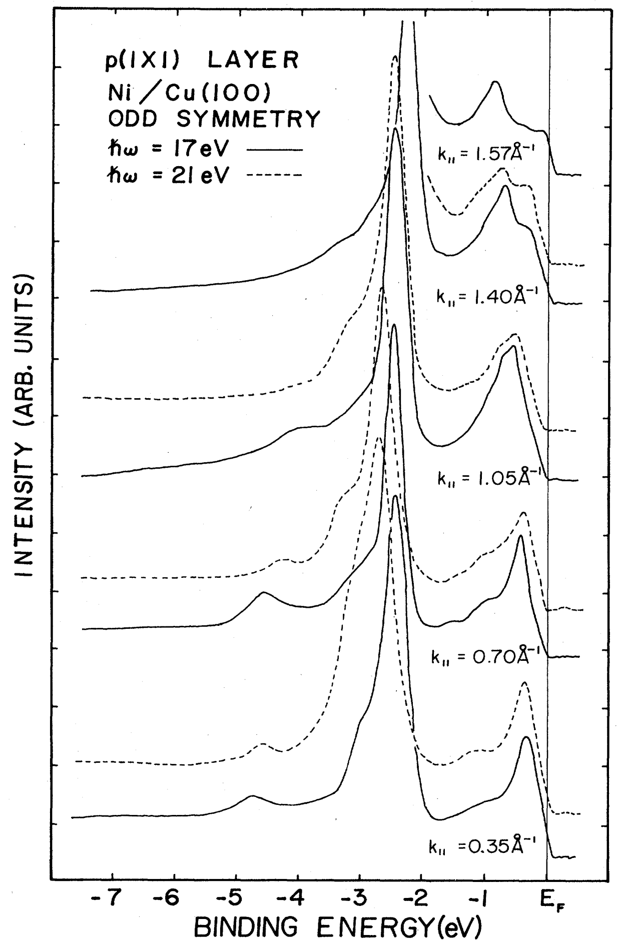

FIG. 1. Angle-resolved EDC's for $p(1\times1)$ Ni/Cu(100) along the $\overline{\Gamma}-\overline{M}$ direction of the two-dimensional Brillouin zone. Features near E_F correspond to odd-symmetry Ni *d* states. Features having a binding energy greater than −2 eV result from Cu *d* states.

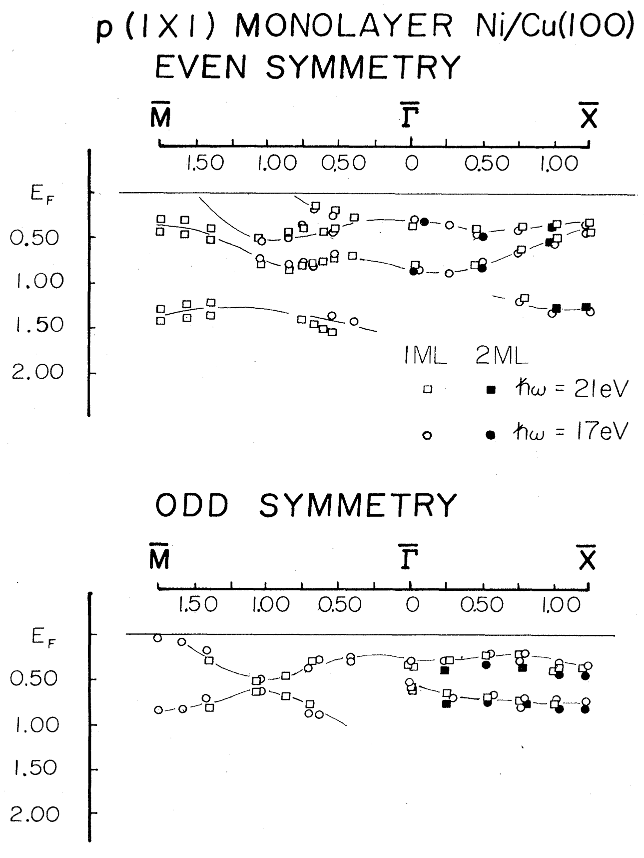

FIG. 2. Dispersion of two-dimensional energy bands for $p(1\times1)$ Ni/Cu(100) along $\overline{\Gamma}-\overline{X}$ and $\overline{\Gamma}-\overline{M}$. Upper panel, even-symmetry states; lower panel, odd-symmetry states. Magnetic exchange splitting is resolved at $\overline{M}$ for even-symmetry states. (ML denotes monolayer.)

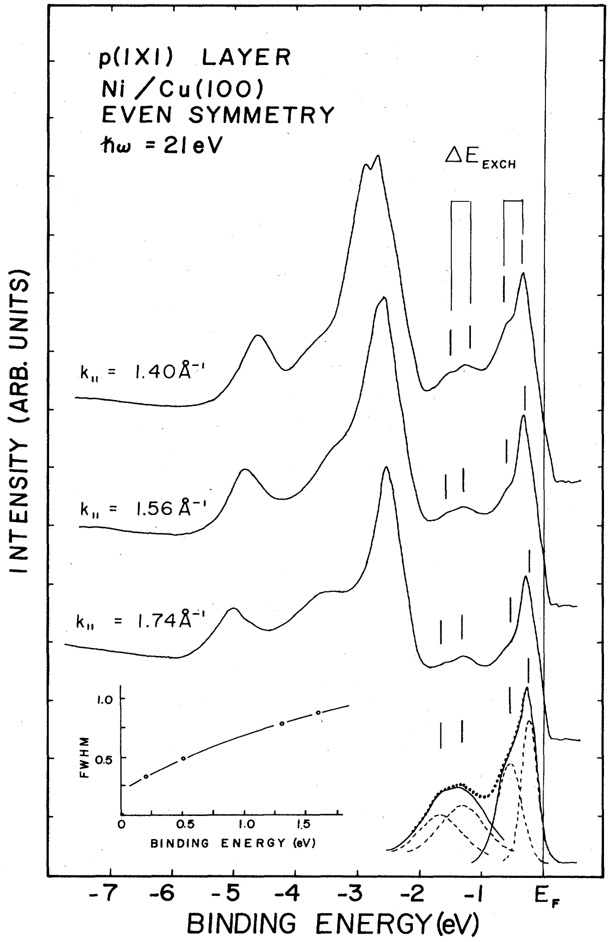

FIG. 3. Angle-resolved EDC's for $p(1\times1)$ Ni/Cu(100). Spectra correspond to even-symmetry states near $\overline{M}$ where the magnetic exchange splitting of two Ni overlayer bands is resolved. Inset at lower left displays the experimentally determined binding energy dependence of the peak width of Ni d-state features in EDC's. Inset at lower right displays Gaussian fit of experimental data used to accurately estimate the exchange splitting. (FWHM denotes full width at half maximum.)

points in the two-dimensional Brillouin zone. Examination of the two-dimensional bands reveals that even-symmetry states near $\overline{M}$ lie near the Fermi energy E_F and are well separated from other states. The highest-lying even-symmetry band at $\overline{M}$ therefore represents a good opportunity to accurately resolve the magnetic exchange splitting.

Figure 3 displays even-symmetry EDC's near $\overline{M}$. Two peaks are clearly resolved near E_F and a second pair of peaks is just resolved at greater binding energy. These peaks were fit by Gaussian functions assuming equal areas for majority and minority spin bands and an intrinsic broadening (as judged from our experimental data) which increases with the binding energy of the state measured from E_F (refer to inset of Fig. 3). The curve-fitting procedure yields an exchange splitting of 0.32 eV in good agreement with the calculations. It is important to note that the existence of a finite exchange splitting, as shown here for the $p(1\times1)$ Ni/Cu(100) monolayer, cannot be regarded alone as an indication of the existence of spontaneous magnetization.[28]

One of the key difficulties in resolving some of the apparent discrepancies among reported calculations has been the lack of relevant experimental data with which to gauge the accuracy of the calculations.[29] The results presented in this paper represent a starting point for reconciling these discrepancies. Additional analysis of our data[30] should provide insight into the perturbation of the Cu sp and d states by one and two layers of $p(1\times1)$ Ni on Cu(100), and could help in improving our understanding the role played by sp-d hybridization in suppressing interface magnetization in this and other transition-metal interfaces. Additional experimental work (in progress) deals with epitaxial layers of Ni on the Cu(111) surface (where quenching of monolayer coverage Ni magnetic moments is predicted[19]) and with the Cu/Ni(100) interface.[31]

It is a pleasure to acknowledge the helpful assistance of Roger Otte and other members of the Synchrotron Radiation Center staff. This work was supported by the National Science Foundation (NSF) (Grant No. DMR-83-04368). The Synchrotron Radiation Center is supported by the NSF.

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