CO Chemisorption on Ni(110): Effect on Surface Magnetism

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(Received 21 October 1985)

The effect of CO chemisorption on the surface magnetism and unfilled electronic structure of Ni(110) is investigated by spin-polarized inverse-photoemission spectroscopy. A saturation in the reduction of the unfilled minority-spin d density of states is observed near 0.5-monolayer CO coverage and attributed to a reduction in the Ni-atom magnetic moments. Transitions into the CO π^* band are also observed with an intensity that increases nearly linearly with coverage. No transference of spin polarization from the Ni substrate to the CO π^* is found.

PACS numbers: 79.60.Gs, 73.20.−r, 75.50.Cc

Because there is strong coupling between the valence electrons in metal atoms of a solid, it follows that adsorption of a molecule on a metal surface should have an effect not only on the electronic structure of substrate atoms directly involved in the chemisorption bond, but on the subsurface and nearest-neighbor atoms as well. Various theoretical studies of chemisorption support this view,[1-3] and the well-known sensitivity of surface states to small amounts of contamination provide experimental evidence for this "through-metal effect" on the surface electronic structure. In ferromagnetic substrates, surface magnetism also exhibits a high sensitivity to contamination.[4-8] Magnetism, when viewed as a macroscopic phenomenon, has its basis in the long-range ordering of the individual magnetic moments of the atoms, whereas the basis for the magnitude of the moments is derived from details of the ferromagnet's valence electronic structure. Early studies[4-6] on the effect of chemisorption on magnetism were not able to distinguish whether the chemisorption-induced reduction in surface magnetism is due to a disruption of the long-range ordering of the magnetic moments or an actual reduction in the moments themselves. Only recently have there emerged experiments of sufficient detail to show the correlated effect that chemisorption has on the substrate magnetic and electronic structure.[7,8] In this Letter, we present the results of measurements on the effect of chemisorption of CO on the surface magnetic and electronic structure of Ni(110) using spin-polarized inverse-photoemission spectroscopy (SPIPES). These measurements indicate that the decrease in surface magnetism that is induced by CO chemisorption is a result of a reduction in the magnetic moments (or net spin) of the atoms rather than a reduction of the exchange coupling leading to a disordering of otherwise unchanged moments.

The SPIPES apparatus and technique have been previously described.[9] For completeness we recap some of the salient features. The probe of this experiment is a spin-polarized electron beam, produced by photoemission from negative-electron-affinity GaAs, and focused onto a uniformly magnetized (single domain) Ni(110) crystal which completes the magnetic circuit of a small C-shaped electromagnet. Some of the electrons absorbed by this crystal radiate a vacuum-ultraviolet photon which we detect using an iodine-and-helium–filled Geiger-Müller counter.[10] This counter has a peak sensitivity for 9.7-eV photons and a 0.7-eV-FWHM bandpass. Spin-resolved spectra are obtained by measurement of the photon counts as a function of electron kinetic energy and separation of the counts according to whether they are produced when the spin polarization is parallel or antiparallel to the crystal magnetization.

The Ni(110) crystal was cleaned by 1-keV Ar-ion bombardment with subsequent flashing to 600 °C. Residual contaminants (C,O,Cl,S) were limited to <0.04 monolayer (ML) total as determined by Auger-electron spectroscopy (AES). Carbon-monoxide exposures were made by direct introduction of the gas into the chamber. Exposures were converted into relative surface coverage by AES measurements of C_{KLL}/Ni_{LMM} peak ratios. Coverage-versus-exposure data obtained in this fashion were compared and found to be in good agreement with earlier thermal-desorption measurements.[11] As will be demonstrated later in this paper, a further check on this scale is provided by the CO-π^* inverse-photoemission intensity measurements.

Inverse-photoemission spectra for the clean Ni(110) surface have been analyzed in some detail.[12-14] For electrons incident at 20° off normal rotating into the surface $\bar{S}$ direction, the arrangement used in this study, the first few electronvolts of the spectra consist of the two transitions indicated in the bulk-band-structure diagram of Fig. 1. Transition A is the dominant of the two and is of particular interest as its final state is the main contributor in the band structure to the minority-spin unfilled density of states that gives rise to the ferromagnetism in Ni. To the extent that chemisorption leaves the initial-state band structure fairly intact, monitoring of this SPIPES transition provides a means for correlating the effect that chem-

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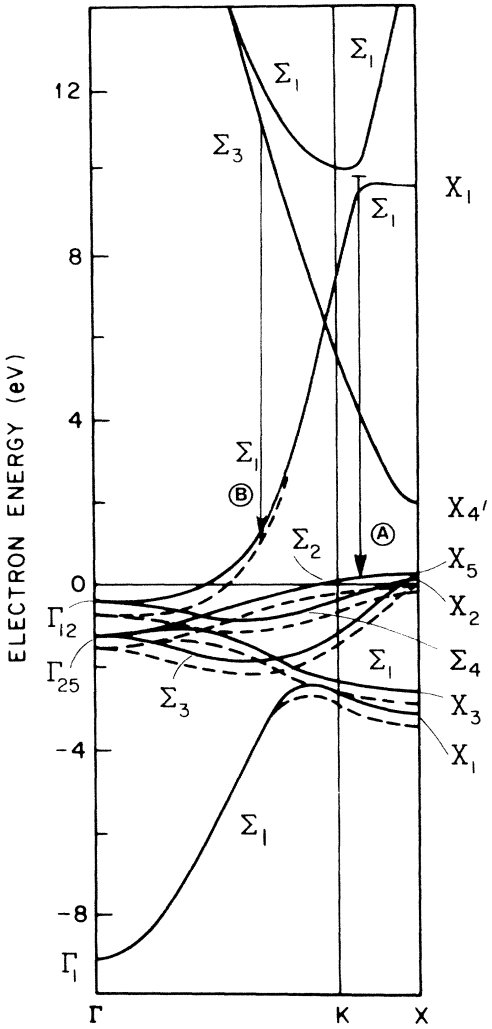

FIG. 1. Band structure of Ni along the direction normal to the Ni(110) surface. The arrows show the two transitions studied in this work. Dashed curves distinguish the majority-spin bands.

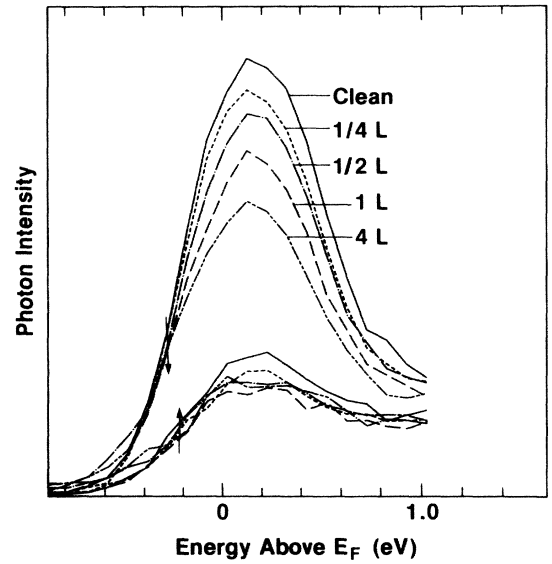

FIG. 2. Spin-resolved inverse-photoemission spectra, $N_\downarrow$ and $N_\uparrow$, for clean Ni(110) and for the surface exposed to $\frac{1}{4}$, $\frac{1}{2}$, 1, and 4 L [1 langmuir (L) $=1\times10^{-6}$ Torr sec] of CO. $N_\uparrow$ and $N_\downarrow$ are the photon intensities which would be obtained with an incident electron beam with 100% spin polarization respectively parallel and antiparallel to the Ni majority-spin density. The abscissa scale refers to the energy of the final state.

isorption has on the surface electronic and magnetic structure. Transition B is also of interest as its final state is a hybrid of the *s,p* band with the exchange-split *d* band. Previous measurements[8] on the effect of oxygen chemisorption on Ni(110) have shown that the intensity of transition A is proportionally reduced by oxygen in the first two stages of chemisorption. In contrast, transition B is unaffected in the initial chemisorption phase of oxygen adsorption and loses intensity only after there is penetration of oxygen below the surface and formation of nickel oxide begins.

Spin-resolved inverse-photoemission spectra for clean Ni(110) and for CO exposures of $\frac{1}{4}$, $\frac{1}{2}$, 1, and 4 L are shown in Fig. 2 in which spectra are presented referenced with respect to the energy of the final state. In this figure, the intensity in the minority-spin ($\downarrow$) channel is due to the previously discussed transition A and a small contribution from transition B, since B is unpolarized, whereas that in the majority-spin ($\uparrow$) channel is due to transition B alone. The smooth decrease in the minority-spin intensity with increasing CO exposure, which is demonstrated in this series of spectra, is similar to the behavior which was previously observed in the earlier study on oxygen chemisorption.[8] However, in contrast to oxygen chemisorption, where the majority-spin peak is still unaffected at 4-L exposure, the majority-spin peak decreases somewhat, on initial exposure ($\frac{1}{4}$ to $\frac{1}{2}$ L) of CO. This behavior was observed reproducibly in several data runs, where the statistical uncertainties in these data were less than the observed changes in intensity. While there are many differences in the bonding of oxygen and CO to metal surfaces, differences in binding sites are one of the most fundamental. In the (2×1) reconstructed phase ($\theta_O \simeq 0.3$ ML), the oxygen occupies long-bridge sites on the Ni(110) surface, whereas for coverages up to 0.5 ML, CO bonds to both on-top and short-bridge sites[15] in about a 5 to 1 ratio.[16] Chemisorption of CO introduces no known reconstruction of the Ni(110) surface, rather $\sim$ 1-ML coverage lifts a 4% contraction of the clean surface layer.[17] Correlation of the adsorption site with the orientation of the orbitals which make up the final state of transition B is complicated by the *s*, *p*, and *d* hybridization. However, the orbital basis of this band near the Fermi level has a large de-

gree of d_z^2 character in the surface frame; i.e., the orbitals are directed nearly perpendicular to the surface. This orientation would be expected to be sensitive to on-top–bonded CO.

Two additional aspects of the effect of CO chemisorption on the inverse-photoemission spectra are shown in the spin-integrated data presented in Fig. 3. Spin-integrated data are generally easier to obtain with good statistics and for this reason were measured over a higher density of exposures and a wider range of final-state energies. The peak in the spectra just above the Fermi level is due to the transitions into the unfilled portion of the Ni d band and is equivalent to the direct sum of the minority- and majority-spin channels presented in Fig. 2. The peak at 3.7 eV above the Fermi level is due to inverse photoemission into the π^* antibonding state of CO. Following the sequence of spectra in Fig. 3, where the spectrum for the clean surface is distinguished by the dashed line, one sees that increasing exposure of CO causes a successive *but saturating* decrease in the d-band intensity, concurrent with a smooth increase in the CO-π^* intensity. At exposures greater than 1.5 L, the d-band intensity saturates at 0.7 of its clean value. By use of an $\sim$5-Å electron mean free path[18] for 10-eV electrons (3–4 atomic layers), this 0.3 reduction in empty density of states corresponds to the quenching of ferromagnetism of one Ni atomic layer. The π^* antibonding level has been previously observed and identified at 3.0 eV above the Fermi level for CO on Ni(111)[19] and at 3.4 eV above the Fermi level for CO on Cu(110).[20] In the present study, the possibility of an additional spin-dependent asymmetry, $(N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$, of inverse photoemission into the π^* band above that present in the inelastic background has been checked for the first time and found to be 0.0 ± 0.02. While there is no resolvable substructure to this peak in our data, some of its large width ($\sim$2 eV) is expected to be due to a π^*+metal and π^*−metal, bonding-antibonding interaction.

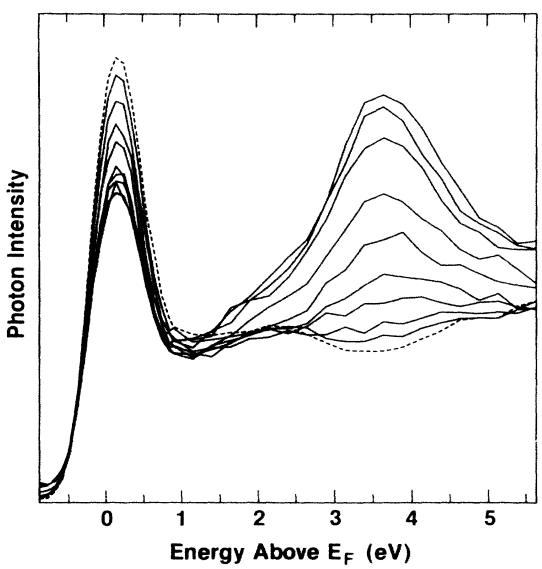

FIG. 3. Spin-integrated inverse-photoemission spectra for clean Ni(110) and Ni exposed to $\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, 1, $\frac{3}{2}$, 2, 3, 4, and 6 L of CO. The clean spectrum is distinguished by the dashed line. The effect of increasing dosages is dimunition of the d-band intensity with a concurrent increase in the CO-π^* intensity.

Since the major contributor to the d-band intensity is minority spin (transition A), and since the changes in the majority-spin channel are minor and restricted to within the first $\frac{1}{2}$ L of CO exposure, monitoring of the spin-integrated inverse-photoemission intensity as a function of CO exposure in this case provides a good measure of the changes in the minority-spin unfilled density of states. This is shown explicity in Fig. 4 where the intensities of inverse photoemission into the spin-integrated d-band, the minority-spin band, and the CO π^* band are plotted versus AES C_{KLL}/Ni_{LMM} peak ratios. The nearly linear relationship of the CO-π^* intensity versus AES signal, as shown in the top half of the figure, provides evidence for the accuracy of the Auger signal as a relative-coverage scale. More importantly, the changes in the d-band intensity (and equivalently the minority-spin-band intensity) are saturating near 1.5-L exposure ($\sim$0.03 on the AES scale) whereas there is still a factor of 2 increase in the π^* intensity with an increase of the exposure to 6 L. On the basis of other thermal-desorption and LEED measurements on the adsorption of CO,[15,21] the AES ratio of 0.03 should be equivalent to 0.5-ML coverage. This saturation in the reduction in surface magnetism at 0.5 ML is in good agreement with earlier ferromagnetic-resonance adsorption measurements on Ni thin films by Göpel,[5] who found that one CO equivalently killed the surface magnetism of two nickel atoms. The mechanism of the decrease of surface magnetism is clarified by the spin-resolved inverse-photoemission data, for if the effect of CO chemisorption was to randomize the orientation of the magnetic moments of Ni atoms adjacent to the CO adsorption site, these randomized moments would give rise to equal intensity in the minority- and majority-spin channels of the SPIPE spectra. We, however, only observe a reduction in the minority-spin intensity, indicating that the reduction in surface magnetism is equivalent to the loss of magnetic moment of two Ni atoms per CO molecule adsorbed.

A filling of the d holes by CO chemisorption is supported by various theoretical studies. Calculations on NiCO have shown that CO causes a change in Ni from a d^9 to a d^{10} configuration.[22] Another study[23] on a more extensive cluster, Ni_{13}+CO, where CO is in a fourfold symmetric site, has predicted changes in the

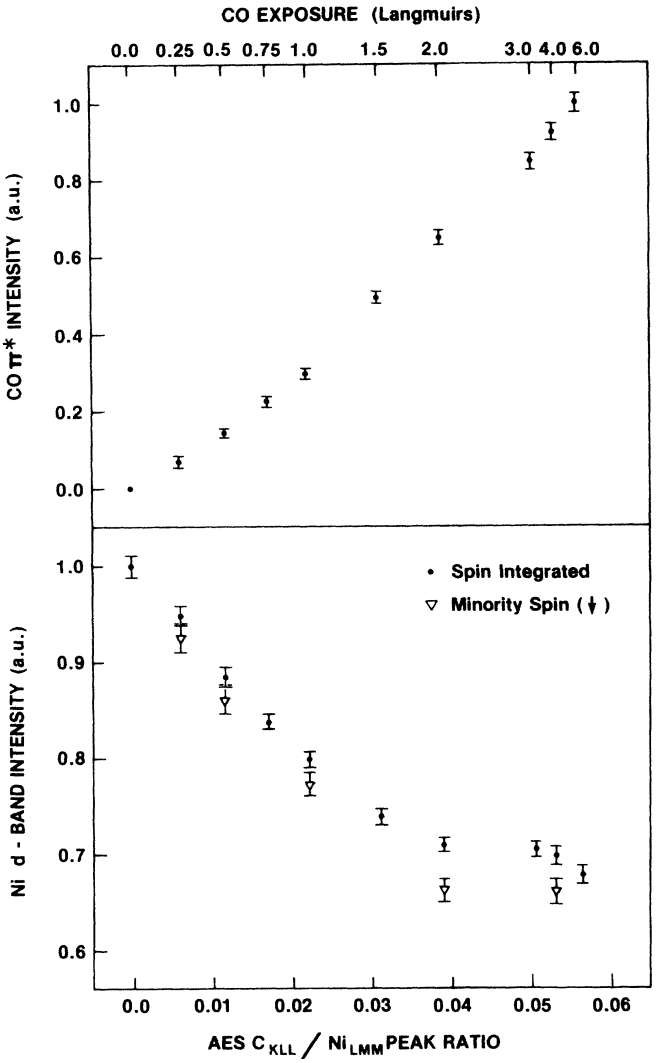

FIG. 4. Intensity of spin-integrated inverse photoemission into the Ni d band and CO π^* band, and spin-resolved inverse photoemission into the minority-spin band, plotted as a function of AES C(272 eV)/Ni(848 eV) peak ratio. Error bars represent 2σ errors from pulse-counting statistics.

moments of all thirteen Ni atoms in the cluster. This theoretical investigation has shown the unfilled minority-spin band to be pushed below the Fermi level by CO chemisorption. In another type of study,[24] all-electron local-density-functional slab calculations of CO on Ni(100) also show a substantial reduction in the unfilled d-density of states on CO chemisorption. Further theoretical studies of on-top CO adsorption on Ni(100) are necessary to clarify the detailed mechanism of Ni magnetic-moment reduction observed in this paper.

We thank B. A. Gurney and W. Ho for making their manuscript available prior to publication. Helpful discussions with W. Goddard, III, N. V. Smith, P. S. Bagus, and N. Shinn are also greatly appreciated. This work was supported in part by the Office of Naval Research, the National Science Foundation, and Consejo Nacional de Ciénca y Tecnológia (Mexico).

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