PHYSICAL REVIEW B VOLUME 32, NUMBER 12 15 DECEMBER 1985

Chemisorption-induced changes in surface magnetism and electronic structure: Oxygen on Ni(110)

A. Seiler, C. S. Feigerle, J. L. Peña,* R. J. Celotta, and D. T. Pierce
National Bureau of Standards, Gaithersburg, Maryland 20899

(Received 28 August 1985)

The effect of oxygen chemisorption on the Ni minority-spin $3d$ holes—and thus the Ni magnetic moment—is measured by spin-polarized inverse photoemission. A dramatic reduction of the minority-spin $3d$ holes is observed, indicating a strong involvement of these states in the chemisorptive bond. This reduction can be explained by a Ni $3d$—O $2p$ interaction which redistributes the density of states; no indication of a reduced exchange splitting is found. Majority-spin *sp* states are shown to be unchanged at coverages below the onset of nucleation and oxide formation.

The relationship between magnetism and chemisorption has traditionally been explored using bulk magnetic measurements and high-surface-area samples.[1] Only a few studies involving surface techniques have been carried out.[2] In this work we investigate the influence of oxygen chemisorption on specific electronic states and on the magnetization at a Ni(110) surface. State-specific information on states near the Fermi energy is crucial for a microscopic understanding of chemisorption. Such information can be obtained from angle-resolved photoemission (occupied states) and inverse photoemission (unoccupied states). In the case of a ferromagnetic material, further information characterizing an electronic state is available if the experiment is also sensitive to the electron spin. In this first application of angle-resolved spin-polarized inverse photoemission spectroscopy (SPIPES) to an adsorbate system, we find that chemisorption of oxygen causes a strong decrease in the number of *d* holes, which assuming the *d* state count is constant, means a decrease in the magnetic moment of the Ni atoms.

The experimental set up for the SPIPES measurements and first results have been described elsewhere.[3–5] In brief, the experiment consists of a spin-polarized electron beam that originates from a GaAs photocathode[6] and is directed on the uniformly magnetized Ni(110) crystal. Some of the electrons undergo radiative transitions which are detected at 45° to the incident-electron beam by a Geiger-Mueller counter[7] which has a bandpass of 0.7 eV centered at 9.7 eV. The sample was cleaned by 1-keV Ar-ion bombardment at 500 °C with subsequent flashing to 600 °C. Surface contaminants were monitored by Auger-electron spectroscopy (AES) and determined to total less than 0.04 monolayers (C,Cl,S) during the experiments. The rate of oxygen uptake, as observed by AES, as well as the occurrence of the 2×1 and 3×1 low-energy-electron diffraction (LEED) structures, were found to be in good agreement with the literature.[8,9] The room-temperature oxidation of Ni takes place in a three-stage process:[8] (i) rapid dissociative chemisorption ($0<\Theta\lesssim0.5$, Θ denotes coverage in monolayers), (ii) nucleation and lateral growth of NiO islands ($\sim0.5<\Theta\lesssim2$), and (iii) slow in-depth growth of the coalesced oxide. The data reported here sample the first two stages of this process.

Several transitions are potentially observable in a SPIPES measurement as illustrated in Fig. 1, which depicts the energy-band diagram[3] for electrons moving normal to the Ni(110) surface. Transition *A* was found to be

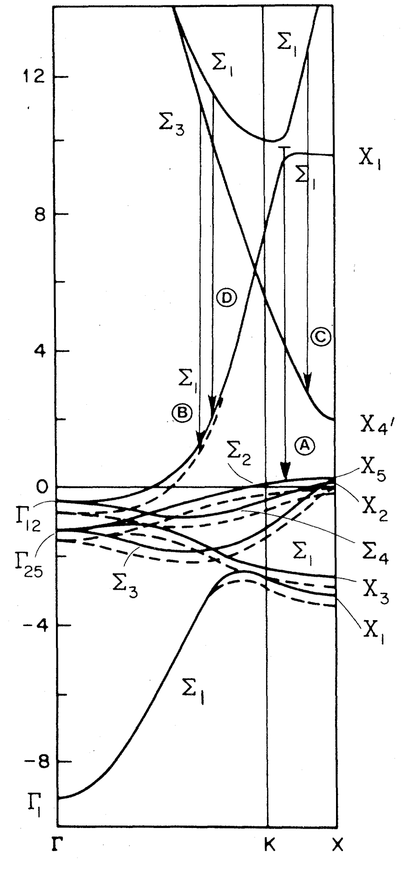

FIG. 1. Band structure of Ni along the direction normal to the Ni(110) surface. The arrows show possible 9.7-eV transition. Dashed curves distinguish the majority-spin bands.

the dominant feature in our first SPIPES experiment[3] on Ni(110). It is highly spin dependent since only minority-spin electrons can make a transition into an empty minority d state. Since these d holes are responsible for the magnetic moment of the Ni atoms, they are of particular interest with regard to chemisorption and its effect on magnetism. In Fig. 2(a) the SPIPES data are shown for clean Ni(110) and for exposures of 1, 4, and 10 langmiurs ($1\ \mathrm{L}=10^{-6}$ Torr sec) of oxygen. The photon intensities for incident electrons having their spin parallel ($N_\uparrow$) and antiparallel ($N_\downarrow$) to the spin of the Ni majority electrons are plotted as a function of the final-state energy with respect to the Fermi level E_F. The main feature of the clean spectra is the prominent minority peak at the Fermi energy which originates from the $\Sigma_1 \rightarrow \Sigma_2$ transition near the X point (transition A in Fig. 1). Owing to the spin resolution it is possible to discern an additional small majority peak at roughly the same energy. The majority peak cannot be due to inhomogeneous sample magnetization, because it behaves differently on oxygen adsorption than the d hole peak and has a different dispersion; it can, in fact, be assigned[10] to transition B of Fig. 1.

When the surface is exposed to oxygen, a very pronounced decrease in intensity of the minority-spin d peak is observed. Perhaps equally striking is the fact that up to an exposure of 10 L the majority peak is not affected. The persistence of this peak on oxygen chemisorption indicates (1) that attenuation effects cannot be the primary reason for the decrease in the minority-peak intensity, and (2) that the bulk band structure explains features of the chemisorbed surface, at least in the lower-coverage range (exposure <10 L, $\Theta<0.6$), even though the surface is known to undergo partial reconstruction.

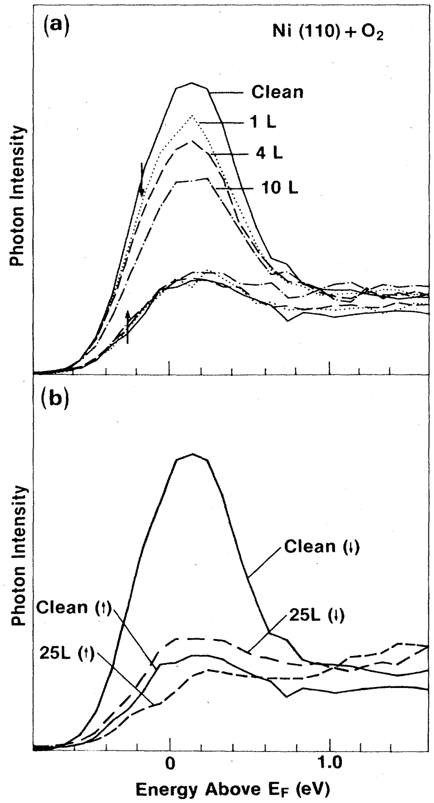

FIG. 2. Spin-resolved photon-intensity spectra, $N_\uparrow$ and $N_\downarrow$, measured at room temperature and 25° angle of incidence of the spin-polarized electron beam. The spectrum of the clean Ni(110) surface is compared to surfaces with oxygen exposures of (a) 1, 4, and 10 L, and (b) 25 L.

A higher exposure of 25 L results in a coverage which is larger than the critical coverage at which oxide formation begins. We observed an additional broad peak located about 3 eV above E_F, which exhibits no spin dependence and which can be associated with the formation of NiO. The majority-spin peak that remained unchanged up to 10 L exposure is finally seen to decrease at 25 L exposure as shown in Fig. 2(b). Since the formation of NiO is certainly linked with dramatic changes in the electronic structure, there could be a correlation between the point at which the majority-peak intensity starts to diminish and the beginning of nucleation and oxide formation. To elucidate this point, the photon asymmetry

$$A=(N_\uparrow-N_\downarrow)/(N_\uparrow+N_\downarrow)$$

has been plotted in Fig. 3 (left-hand scale) along with the intensity of the minority-spin d peak (right-hand scale), both at ~ 0.1 eV as a function of coverage, expressed by the O(511 eV):Ni(848 eV) AES peak ratio. Since the minority-peak intensity decreases linearly with coverage, the point at which the majority-spin peak starts to be affected is manifested as a break in the asymmetry curve. This break occurs at 10 L ($\Theta\sim 0.6$) and correlates well with the range $0.40<\Theta<0.66$ for the onset of the nucleation and growth regime as cited in the literature.[8,9]

The higher-coverage spectra also allow us to estimate the relative contributions to the spectra from transitions at the surface and in the bulk. The minority-spin d hole peak almost completely vanished at an exposure of 25 L, which implies little contribution from the Ni bulk to the minority peak. The oxidation is known to saturate at ~ 2 layers[11] of NiO. These facts imply a probing depth or

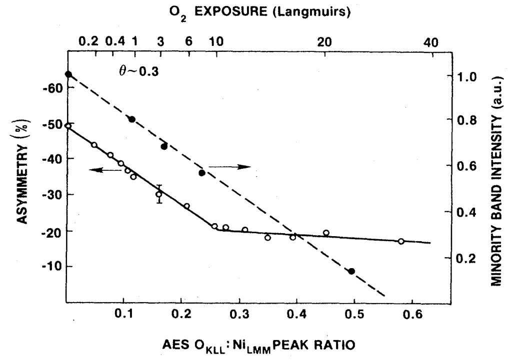

FIG. 3. Asymmetry parameter $A=(N_\uparrow-N_\downarrow)/(N_\uparrow+N_\downarrow)$ (left-hand scale) and minority-band intensity $N_\downarrow$ (right-hand scale) as a function of the Auger [O(511 eV)/Ni (848 eV)](dN/dE) peak-to-peak ratio. The coverage scale in monolayers was set taking $\Theta=0.3$ at 1 L exposure, where the (2×1) pattern is observed (Ref. 8).

mean free path of 3—5 Å.

The data show that the unfilled d states are strongly affected by the formation of the chemisorption bond. The effect of chemisorption is not, however, explainable based on simple chemical-valency arguments, which would predict an increase in the unfilled-d-electron density of states. The reduction in surface magnetism that is precipitated by the oxygen chemisorption is also not due to a reduction in the exchange splitting in the form of a rigid shift of the d bands, which would be manifested by a SPIPES spectrum with an equal amount of up- and down-spin holes. The observed reduction in the number of d holes can be best explained by the Ni $3d$—O $2p$ interaction and the resulting rearrangement of the density of states. Theoretical studies of the related system C(2×2)O/Ni(100) by Liebsch[12] and by Wang and Freeman[13] predict substantial changes in the local density of states near the Fermi level upon chemisorption. New bonding states at ~6 eV below the Fermi level and antibonding states just above the Fermi level are formed due to the Ni $3d$—O $2p$ interaction. These states are inherently atomic and sharp, but can be broadened by hybridization with the Ni *sp* band. The antibonding states have been previously observed as weak spectral features in angle-integrated inverse photoemission of oxygen on Ni(100) and Ni(111).[14] Due to the anisotropy of the surface, these states are further split into O $2p_z$— and o $2p_x,p_y$—derived states. This splitting has been empirically observed[15] in light-polarization-dependent, angle-resolved, inverse-photoemission measurements of oxygen on Ni(111). We, however, do not observe these antibonding levels in our spectra, presumably due to the weakness of the transitions, possible broadening by hybridization with the Ni *sp* band, and an experimental arrangement which favors accepting light polarized in the plane of the sample.

Calculations also show that there is substantial shifting of the density of states within the d band and even redistribution of state density between the Ni d bands brought on by oxygen chemisorption. It is to these changes that the SPIPES measurement has shown particular sensitivity. Liebsch has found that the interaction of the O $2p_z$ and the d bands changed the density of states so that the partial-wave projections for $3d_{z^2}$ and $3d_{xy}$ components are very similar, whereas for the clean surface the density of states for these components are quite distinct. Such a coupling provides a mechanism by which the minority-spin band of Ni(110) is drawn below the Fermi level by oxygen chemisorption. A similar mechanism has been shown in a recent spin-dependent calculation[16] for CO on Ni clusters which demonstrates that CO induces a transfer of electrons from the filled d levels into the unfilled minority-spin levels and a commensurate reduction in the magnetic moment at the Ni atoms. In conclusion, we have shown that the SPIPES spectra provide detailed information on the chemisorption-induced changes in surface magnetism and electronic structure and give direction for the further theoretical and experimental work that will be required for a complete understanding of the intricacies of these phenomena.

ACKNOWLEDGMENTS

We wish to acknowledge helpful discussions with N. V. Smith. This work was supported in part by the Office of Naval Research, and by the National Science Foundation (U.S.) and Consejo Nacional de Ciéncia y Tecnológia (CONACyT, Mexico).

---

[*] Permanent address: Centro de Investigacion y de Estudios Avanzados del Instituto Politécnico Nacional, Apartado Postal 14-740, México 14, Distrito Federal, Mexico.

[1] See, e.g., P. W. Selwood, *Chemisorption and Magnetization* (Academic, New York, 1975).

[2] M. Landolt and M. Campagna, Phys. Rev. Lett. **39**, 568 (1977); E. Eichner, C. Rau, and R. Sizmann, J. Magn. Magn. Mater. **6**, 208 (1977); R. J. Celotta, D. T. Pierce, and G. C. Wang, in Proceedings of the 4th International Conference on Solid Surfaces and 3rd European Conference on Surface Science, Cannes, 1980, p. 1045 (unpublished).

[3] J. Unguris, A. Seiler, R. J. Celotta, D. T. Pierce, P. D. Johnson, and N. V. Smith, Phys. Rev. Lett. **49**, 1047 (1982).

[4] A. Seiler, C. S. Feigerle, J. L. Peña, R. J. Celotta, and D. T. Pierce, J. Appl. Phys. **57**, 3638 (1985).

[5] C. S. Feigerle, A. Seiler, J. L. Peña, R. J. Celotta, and D. T. Pierce, J. Vac. Sci. Technol. A **3**, 1487 (1985).

[6] D. T. Pierce, R. J. Celotta, G. C. Wang, W. N. Unertl, A. Galejs, C. W. Kuyatt, and S. R. Mielczarek, Rev. Sci. Instrum. **51**, 478 (1980).

[7] G. Denninger, V. Dose, and H. Scheidt, Appl. Phys. **18**, 375 (1979).

[8] P. H. Holloway, J. Vac. Soc. Technol. **18**, 653 (1981), and references therein.

[9] S. Masuda, M. Nishijima, Y. Sakisaka, and M. Onchi, Phys. Rev. B **25**, 863 (1982).

[10] A. Seiler, C. S. Feigerle, R. J. Celotta, D. T. Pierce, and N. V. Smith (unpublished).

[11] K. H. Rieder, Appl. Surf. Sci. **2**, 74 (1978).

[12] A. Liebsch, Phys. Rev. B **17**, 1653 (1978).

[13] C. W. Wang and A. J. Freeman, Phys. Rev. B **19**, 4930 (1979).

[14] H. Scheidt, M. Glöbel, and V. Dose, Surf. Sci. **112**, 97 (1981).

[15] F. J. Himpsel and Th. Fauster, Phys. Rev. Lett. **49**, 1583 (1982).

[16] F. Raatz and D. R. Salahub, Surf. Sci. **146**, 1609 (1984).