Connection between surface magnetism and electronic structure of oxygen on Ni(110) (invited)

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The *d*-band holes which give rise to ferromagnetism in Ni can be directly observed by spin-polarized inverse photoelectron spectroscopy (SPIPES). Only incident electrons polarized in the minority spin direction can fall into unfilled minority spin states and radiate a detected photon. On dissociative chemisorption of O_2 we observe a reduction in the number of minority spin *d* holes. It is this change in electronic structure which gives rise to a decrease in magnetization. A background of minority and majority spin states remains essentially unchanged. Further exposure to oxygen causes formation of NiO; the surface magnetization goes to zero, and a completely different SPIPES spectrum is observed. The relative importance of *d* electrons and *s, p* electrons in chemisorptive bonding on Ni has been much discussed. These data suggest that the *d* states interact strongly with the oxygen and that this interaction has a profound influence on the surface magnetism.

The differences between the magnetic properties of a bulk ferromagnet and those at a surface or interface are intimately related to differences in electronic structure. This is particularly true for Ni, an itinerant ferromagnet, where the magnetism arises from exchange split *d* electron states which are very sensitive to local environment. We have used spin-polarized inverse photoelectron spectroscopy (SPIPES) to investigate the electronic structure and surface magnetism of Ni and the changes that are induced by chemisorption. In this paper we summarize the results of our study of room-temperature adsorption of oxygen on the Ni(110) surface; a more detailed description will be presented in a forthcoming publication.[1]

The majority (up) spin *d* states of Ni lie below the Fermi level and are filled, whereas the minority (down) spin *d* states are only partially filled leaving approximately half an unfilled state (*d* hole) per Ni atom. While the *d* electron states are clearly central to ferromagnetism in Ni, their role in chemisorption bonding is much disputed and discussed in the literature with estimates of the importance of the *d* electrons ranging from minor[2] to predominant.[3] Thus, if we focus on the unfilled minority *d* states as we can do in the spin-polarized inverse photoemission experiments described below, and use existing theories to make predictions of the changes in the spectrum of *d* holes to be expected on chemisorption of oxygen, we arrive at several possibilities:

(1) The *d* electrons are only very weakly involved in the bonding, and no significant change should be expected in the spectrum of *d*-hole states or the surface magnetization.

(2) There is a reduction in the exchange splitting at the surface such that there is an equal number of up and down spin holes (which could be observed in a SPIPES spectrum). The surface Ni atoms become magnetically dead, and one has a paramagnetic surface.

(3) There is a transfer of Ni *d* electrons to the oxygen creating holes which would be observed in the spectrum. The magnetization would increase or decrease depending on the relative numbers of minority and majority spin electrons transferred. However, the local density of states of the metal atoms could also be affected by a hybridization of the adatom and metal atom orbitals.

(4) There is a decrease in the *d*-hole spectrum and an apparent "filling" of these states along with a decrease in the magnetization. Molecular orbital calculations of NiN_2 and NiCO show that a $3d\,^{10}$Ni configuration (filled hole) is preferred.[4] The suppression of the magnetization at interfaces of Ni with simple metals has been attributed to *sp-d* hybridization[5]; similar effects in chemisorption could change the nature of the *d*-hole spectrum and decrease the magnetization.

Although the above descriptions oversimplify the possibilities as discussed in the references cited, they serve to illustrate the diversity of viewpoints.

The relationship between magnetism and chemisorption has been traditionally studied by bulk magnetization techniques on high-surface-area samples.[6] In only a few cases have true surface techniques with spin sensitivity been applied to this problem. Spin-polarized field emission[7] studies of Ni(100) and electron capture studies[8] of Ni(110) both show a drastic decrease in the surface magnetization with hydrogen adsorption. The asymmetry in polarized electron scattering[9] decreases with oxygen chemisorption on the Ni(110) surface, indicating a decrease in the surface magnetization with exposure. Surprisingly, the spin polarization measured for Ni(110) in threshold photoemission is quite insensitive to oxygen adsorption.[10] However, the change in electronic structure such as we can measure with SPIPES has not been previously investigated nor correlated with changes in surface magnetization.

Holloway[11] has reviewed the extensive investigations of the oxidation of Ni which proceeds in three stages—chemisorption, oxide nucleation and growth to coalescence, and thickening of the coalesced oxide. We are concerned with the first two stages. The clean Ni(110) surface was obtained by 1-

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keV Ar ion bombardment at 500 °C with subsequent flashing to 600 °C. The contaminants (C,Cl,S) on the clean surface were measured by Auger spectroscopy and totaled to less than 0.04 monolayer. Oxygen chemisorbs dissociatively, and the intial uptake is rapid. Consistent with the literature,[11–13] at an exposure of 0.8–1.2 L (1 L = 10^{-6} Torr sec), we observed a (2×1) LEED pattern followed by a mixed (2×1) and (3×1) phase up to an exposure of 3 L where a (3×1) pattern occurred.

The relative coverage of oxygen as a function of exposure was determined by measuring the O(511 eV)/Ni(848 eV) Auger peak height ratio. The absolute coverage was set to be $\theta = 0.3$ monolayer at 1 L where the (2×1) pattern is observed, in accordance with values reported in the literature.[12–14] Thus the exposures of 1, 4, and 10 L, at which we measured the SPIPES spectra, correspond to coverages of approximately 0.3, 0.45, and 0.62 monolayers of oxygen. There is some controversy about where the chemisorption stage ends and oxide nucleation begins, with most estimates ranging from $\theta = 0.44$ to 0.66 monolayer.[11] However, ion scattering evidence for the displacement of Ni atoms at a coverage of 0.3 monolayer was associated with the onset of oxidation.[12] Further studies of the change in surface magnetization and electronic structure as a function of oxygen coverage are in progress, from which we hope to be able to shed light on this controversy about models of the oxidation process.

Inverse photoemission allows the investigation of unoccupied electron states; in particular it makes accessible information about the energy region between the Fermi level and the vacuum level that cannot be obtained otherwise. An electron incident on the material with energy E_0 can undergo a direct radiative transition to an energy E giving off a photon of energy $\hbar\omega$. Since the initial energy and the photon energy are known, information on the states at an energy $E = E_0 - \hbar\omega$ above the Fermi level is obtained. The electrons are incident on the material in a well-defined beam, and, consequently, they probe electron energy levels in the solid associated with electrons moving in a well-defined direction. The energy levels, or band diagram, for electrons moving normal to the Ni(110) surface is shown in Fig. 1. The exchange splitting of the bands is indicated by solid lines for minority spins and dashed lines for majority spins.[15]

The spin dependence of the energy levels can be investigated if the incident beam is spin polarized. In particular, the transition whose spin dependence this investigation is concerned with is indicated by the arrow in Fig. 1. The initial state of this 9.7-eV transition contains both spins; however, the final state is solely of minority spin character so only incident minority spins can make a transition into it and thereby create a 9.7-eV photon. In our experiment a GaAs spin-polarized electron source[16] is used to produce an incident polarized electron beam. The photon detector is an iodine- and helium-filled Geiger-Müller counter[17] with a photon energy bandpass of 9.7 ± 0.35 eV created by the iodine ionization threshold and the UV transmission cutoff of the CaF_2 window. The first SPIPES measurements were made on a clean Ni(110) surface; the experimental apparatus was described more completely in that publication.[15]

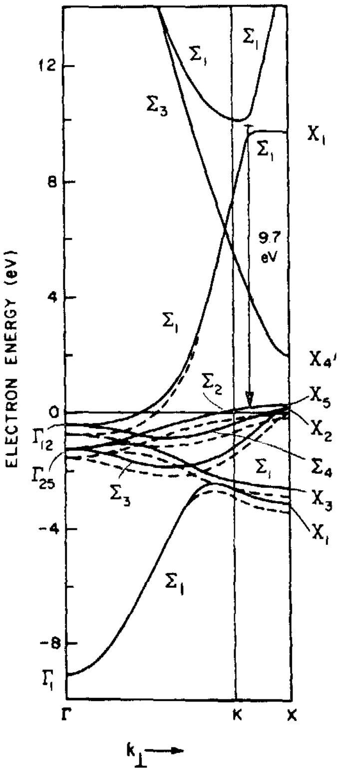

FIG. 1. Band structure of Ni along the ΓKX direction showing a possible radiative transition at $\hbar\omega = 9.7$ eV for electrons incident normally on Ni(110). The dashed curves distinguish the majority spin bands.

The SPIPES spectra for clean Ni and Ni exposed to 1, 4, and 10 L of oxygen are shown in Fig. 2. The photon intensity for incident minority(↓) and majority (↑) spins is plotted as a function of the final-state energy with respect to the Fermi level E_F. The data for Fig. 2 are for an angle of incidence of 20°. At normal incidence, the transition of interest depicted

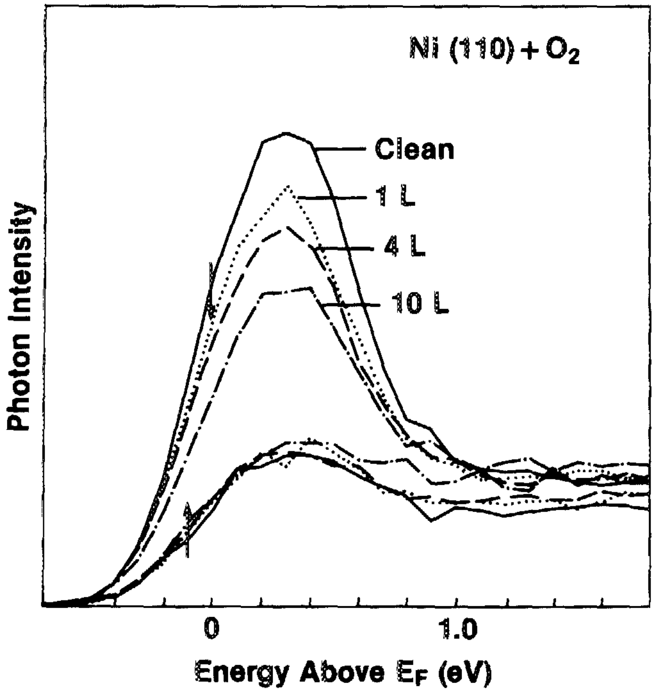

FIG. 2. Inverse photoemission spectra for clean Ni(110) and with oxygen exposures of 1, 4 and 10 L (1 L = 10^{-6} Torr sec). At each exposure there are two spectra, one when the incident electron is in the majority spin direction (↑) and one when it is in the minority spin direction (↓).

by the arrow in Fig. 1 is symmetry forbidden. The electron beam intensity and detector efficiency have been improved so that count rates are over 20 times higher than for our first measurements.[15] At the same time the background intensity is greatly reduced. The remaining background is believed related to electron-hole pair production by the incident electrons before photon emission; this contribution to background is zero at threshold and increases with energy above E_F.[18] With this improvement in the peak-to-background ratio a small unexpected peak just above E_F is observed in the photon intensity due to incident majority spin electrons. (A similar peak in the minority spectrum could be masked by the large d-hole peak.) In Fig. 1 there are allowed 9.7-eV transitions to final s, p-like states but these lie 2–3 eV above E_F. This peak that is observed with majority spin incident electrons may be due to transitions to s, p-like final states which would be apparent in a band diagram appropriate for our angle of incidence.[19]

The striking change that takes place on chemisorption of oxygen is the decrease in the minority spin photon intensity peak corresponding to electron transitions to the d-hole states just above E_F. Perhaps equally striking is the fact that there is no change in the small majority spin peak up to an exposure of 10 L. Careful measurements were made of the majority spin peak to ascertain that changes proportional to those of the minority peak would be well above the noise. To the extent that transitions to both the minority and majority spin peaks have the same initial state, the absence of change in the majority peak rules out initial-state changes being responsible for changes in the minority peak. We believe that the change in the minority spin peak is due to a change in the final state, that is, to an apparent filling of the d holes.

The rate of decrease of the minority peak is moderated by mean-free-path effects. The mean free path for electrons with energy 10 eV with respect to E_F is estimated to be ~ 5 Å, which is four atomic layers for Ni(110).[20] On the average about 20% of the incident electrons interact with the first layer. There are also contributions to the spectrum by photons resulting from electrons interacting with subsurface Ni layers which are initially unperturbed by the oxygen.

We have also made measurements at higher coverages which are qualitatively different. Data at an exposure of 25 L (estimated coverage $\theta \simeq 1.3$) began to show some decrease in the majority peak as well. At very high exposures of a few hundred langmuirs and especially for increased temperature (~ 200 °C), a thick oxide is formed. The structure within 1 eV above E_F disappears, and there is a broad NiO peak about 3 eV above E_F. The spectra for majority and minority spins are identical, as expected for an antiferromagnetic oxide.

Referring back to the four predictions outlined above, it is clear that there is a significant change in the empty d-state spectrum on oxygen chemisorption. There is no evidence for reduced exchange splitting leading to an equal number of up and down spin holes. There is also no evidence for the net transfer of d electrons to oxygen such that the number of holes is increased. A hybridization of the d states with sp states leading to states which are so spread out in energy that the change is below our detection limit cannot, however, be ruled out. We conclude that there is an apparent filling of the empty d states and that those same states that are crucial to ferromagnetism in Ni are also very active in the chemisorption bonding.

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