Chemisorption of H on Magnetic Ni(001)

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A theoretical investigation of an ordered $p(1\times1)$ H overlayer on Ni(001) shows a marked reduction of the surface Ni moment to $\sim 0.2\mu_B$ (which at room temperature gives the impression of a "dead" layer) and the formation of a covalent-metallic bond between H and Ni. These results, along with the calculated equilibrium properties and single-particle spectrum, are discussed and compared to experiment.

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While the adsorption of hydrogen on metals has been extensively studied in recent years,[1] there have been relatively few investigations of the magnetic properties of adsorbates. This is surprising since iron and nickel are important catalysts and hydrogen is in many ways the simplest adsorbate. Hydrogen is known to reduce the magnetic moment at Ni surfaces,[2] yet the well-known magnetic surface state on Ni(001) is unaffected by hydrogen adsorption.[3] In order to study the interplay of magnetism and chemisorption, we present the first self-consistent spin-polarized calculations of the electronic and magnetic structure of hydrogen chemisorbed on a ferromagnetic Ni(001) substrate.

By now there is a good theoretical understanding of the effect of the surface on the electronic and magnetic properties of Ni(001) based on first-principle calculations.[4,5] The recent theoretical studies of H on Ni(001),[6–9] on the other hand, have emphasized global features of the bonding (e.g., bond lengths and cohesive energies) and ignored the magnetism. In this paper we not only determine equilibrium properties, but also discuss how the H modifies the surface magnetism and charge density of the Ni(001) surface.

The surface is modeled by a seven-layer Ni(001) film with an ordered $p(1\times1)$ monolayer of H on each side in the fourfold hollow. [The $p(1\times1)$ is the only ordered overlayer observed in He diffraction.[10]] The (local) spin-density functional equations[11] are solved by use of the highly accurate full-potential linearized augmented plane wave method.[12] The H-Ni bond length was varied between 1.78 and 1.85 Å and the equilibrium properties were determined both from the total energy[13] and the force.[14] The calculated bond length, $d_{\text{Ni-H}}$, is 1.80 Å (0.69 a.u. above the outermost Ni plane) and is shorter than that of bulk nickel hydride (1.86 Å). [As is typical of local-density approximation calculations,[13] the cohesive energy of 3.2 eV per H atom (including zero-point motion) is overbound by ~ 0.5 eV compared to experiment.[15]] Although our $d_{\text{Ni-H}}$ is significantly shorter than the 1.95–2.0 Å value deduced by Rieder and Wilsch,[10] the overlapping atomic density model and the uncertainty in the scattering potential used in their analysis could account for the difference: Neglecting the self-consistent smoothening of the density has the effect of increasing the deduced $d_{\text{Ni-H}}$. (The same arguments apply to the $d_{\text{Ni-H}} = 1.92$ Å value found in Ref. 7.) Our value is further supported by our calculated vibrational frequency of 82 meV, in good agreement with the experimental value[16,17] of 74 meV, and the theoretical work of Upton and Goddard[6] and Umrigar and Wilkins.[9] (The slightly shorter $d_{\text{Ni-H}}$ found in these calculations is consistent with their neglect of magnetic ordering.) Finally, the change in work function $\Delta\phi$ from our value of 5.36 eV for Ni(001) is a sensitive function of $d_{\text{Ni-H}}$. Experimentally,[15] $\Delta\phi = 0.17$ eV for a coverage of ~ 0.5 monolayer; our calculated increase of ~ 0.4 eV for a full monolayer is consistent with this value. Larger values of $d_{\text{Ni-H}}$ are clearly incompatible with the data: Already for $d_{\text{Ni-H}} = 1.85$ Å, we find $\Delta\phi = 0.7$ eV.

In order to display the polarization of the density that occurs as a result of H adsorption (and gives rise to $\Delta\phi$), the difference between the H/Ni(001) density and the superposition of the densities appropriate to Ni(001) and atomic H is given in Fig. 1. The polarization of the density, as expected, is localized to the surface region and shows the importance of correctly including (as done here[12]) the nonspherical contributions to the density and potential. There is a clear enhancement of the charge along the Ni-H bond indicating substantial covalency. This bonding is the essential reason for the reduction in the magnetic moment at the surface—formation of a Ni-H bond pairs electrons.

The spin density (Fig. 1) is strongly reduced at the surface, yielding a moment of $\sim 0.2\mu_B$ per Ni atom, while below the surface it rapidly approaches bulklike behavior. (Figure 1 emphasizes the regions of low spin density. The main contributions to the moments come from regions of large spin density around the Ni atoms: A measure of the moment on a Ni site is the area inside the uppermost positive contour. Hence one sees that there is a reduction of the surface moment.) The spin density around the H site (marked by

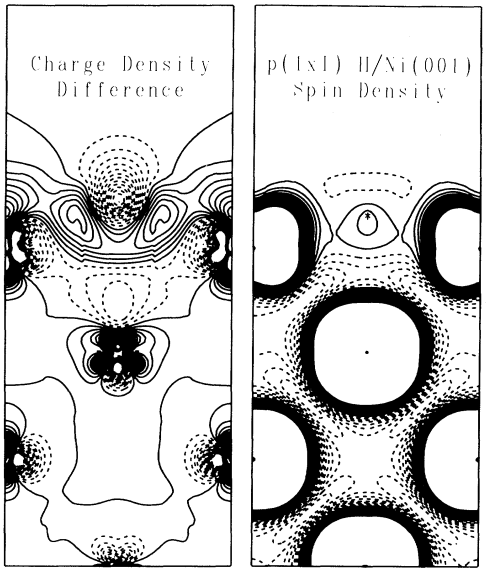

FIG. 1. Charge-density difference between H/Ni(001) and the superposition of Ni(001) plus atomic H (contour spacing of 10^{-3} e/a.u.^{3}) and the H/Ni(001) spin density (contour spacing 10^{-4} a.u.$^{-3}$). Negative contours are dotted and the position of the H is marked by an asterisk.

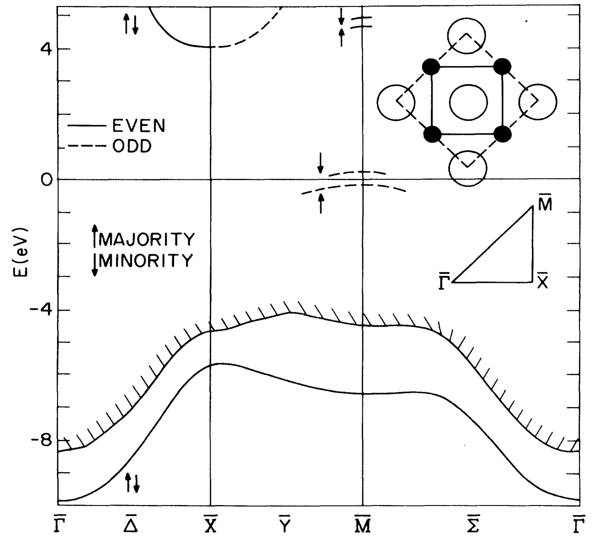

FIG. 2. Energies of selected $p(1\times1)$H/Ni(001) surface states labeled by spin and mirror symmetry. The bottom of the Ni bands is hatched and the H is at the origin of the coordinate system. Note that our coordinate system shown in the inset is rotated relative to the conventional cube axes which relabels some states, e.g., $d_{xy} \leftrightarrow d_{x^2-y^2}$.

an asterisk) is highly nonspherical with regions of both positive and negative densities which integrate to a near zero value about the H. At the H nucleus itself, the spin density is positive—unlike the negative contact term found for H in the bulk[18]—because of the reduced symmetry at the surface.

From the reduced moment at the surface and the changes in the electronic structure at the surface, one would expect that those single-particle states localized in the surface region should be modified. The reason that the magnetic surface state at $\bar{M}$, which is composed of $d_{x^2-y^2}$ orbitals (in our coordinate system), is unaffected by H is simply that this state and the H level belong to different irreducible representations, cf. Fig. 2; a simple way to see this is to note that the H sits between the lobes of this state. That the exchange splitting is not reduced is due to the localized nature of the planar $d_{x^2-y^2}$ orbitals of this state and its position near E_F: The calculated exchange integral of this state is so much larger than that of bulk Ni[19] that the Stoner criterion for the surface is satisfied.[20] This implies that the surface will remain ferromagnetic, albeit with a much reduced moment.

The other surface features in Fig. 2 are described as follows. The energy of the unoccupied surface state around $\bar{X}$ drops by 0.5 eV (relative to E_F)—the H has little effect on states with odd mirror symmetry other than shifts. Through direct interaction, however, the H induces a localized non–exchange-split state below the Ni bonds. The relative position of this band below the Ni continuum increases with decreasing $d_{\text{Ni-H}}$, as expected for the bonding combination of Ni and H states; the corresponding antibonding combination is most clearly seen at $\bar{M}$, 4.5 eV above E_F. At $\bar{\Gamma}$ the H-induced states are a mixture of H and Ni s, while at $\bar{M}$ they are H-s–Ni-3d_{xy} hybrids, clearly showing that the bonding with H involves both Ni s and d orbitals. In calculations of the clean surface,[4,5] the Ni 3d_{xy} states at $\bar{M}$ form a surface resonance 3 eV below E_F due to the same potential-shift mechanism responsible for the magnetic surface state. Unfortunately, this surface state at $\bar{M}$ has not been observed in photoemission[3] for either the clean or the H-covered surface. We speculate that there may be a quasiselection rule which greatly reduces the intensity. This point requires further study.

The increased moment on the clean Ni surface can be viewed[5] as a consequence of the band narrowing and an upward electrostatic shift which occurs to maintain charge neutrality, resulting in a decrease of the minority population. (Without a shift, the minority and total charge would increase.) For the H-covered surface, the bands still narrow, but because of Ni-H hybridization, charge neutrality is maintained without an electrostatic shift or charge transfer. Hence, the decreased magnetic moment can be thought of as a minority band-filling effect. However, this is not the same as the simple picture in which the extra band resulting from the H-Ni interaction appears above E_F and the extra electron just fills the top of the Ni d band which results in no moment at the surface. Instead there are significant changes to the band structure and density of states in the *d* bands on H adsorption. Our mechanism is supported by the calculated 3*s* initial-state core-level shifts: There is no minority shift while the majority shift, as always for a strong ferromagnet, is determined by the exchange splitting. This latter shift of 0.5 eV and the hybridization of the H *s* with the filled majority Ni *d* band act to decrease the majority *d* character inside the surface Ni sphere by 0.13 electron. Combined with an increase of 0.25 minority *d* electron due to band narrowing, this results in a decrease in the moment to $\sim 0.2\mu_B$. These results give a rather simple physical picture of the reduction of the surface moment and should apply to other adsorbates on Ni as well.

All of these results apply to zero temperature. In order to investigate the temperature dependence, we have utilized a Heisenberg model treated in mean-field approximation[21] with the parameters fitted to our $T=0$ calculations. The results are shown in Fig. 3 for $T=0$ and 300 K. The room-temperature (300 K) results show an overall decrease in the magnetization relative to the $T=0$ results, with the surface moment decreasing more rapidly than the bulk. For the clean surface, the surface moment is still approximately the same as the bulk, whereas for the H-covered surface, the moment is now only ~ 0.1 of the $T=0$ bulk value. Hence at room temperature, H adsorbed on a Ni surface would give the appearance of a magnetic "dead" layer; these results support the suggestion[22] that the original observation[23] of "dead" layers was due to H contamination.

The results presented here demonstrate the interplay between the electronic and magnetic properties of H adsorbed on a magnetic substrate and allow for rather simple interpretations of the physics. In general, our results are in good agreement with a variety of experiments. Some questions that remain to be answered include the origin of the discrepancy between the photoemission and theoretical results and how the H-metal interactions vary with coverage.

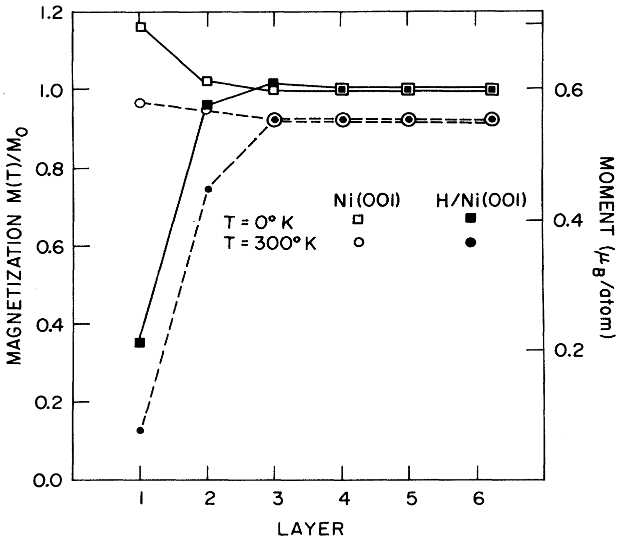

FIG. 3. Layer magnetic moments for Ni(001) and H/Ni(001).

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