PHYSICAL REVIEW B VOLUME 53, NUMBER 1 1 JANUARY 1996-I

Magnetic consequences of NO chemisorption on (100) metal surfaces

K. C. Hass
Physics Department, Ford Motor Company, SRL MD-3028, Dearborn, Michigan 48121-2053

M.-H. Tsai
Physics Department, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China

R. V. Kasowski
Central Research and Development Department, E. I. DuPont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

(Received 21 September 1995)

The magnetic properties of NO overlayers on a variety of ferromagnetic and paramagnetic (100) metal surfaces are calculated within the local-spin-density approximation. Bridge-site adsorption results in negligible spin densities in all cases on Rh, Pd, and Pt, and strongly suppresses the surface magnetic moments of Ni. Atop-site adsorption yields more complicated behavior, including residual NO magnetic moments on Pd (100) monolayers and induced ferromagnetism on thicker Pd and Pt slabs.

It is well established that the adsorption of CO on Ni surfaces[1] and clusters[2] significantly reduces the magnetic moments of the Ni atoms to which the CO bonds. While some evidence exists for similar effects in other systems,[3,4] many fundamental aspects of the interplay between adsorbate bonding and transition-metal magnetism remain unclear. In particular, relatively little is known about the magnetic properties of chemisorbed systems involving *paramagnetic* molecules, such as NO.[5,6] Here we begin to address this issue theoretically by presenting first-principles, local-spin-density approximation[7] (LSDA), pseudofunction[8] calculations for NO overlayers on a variety of ferromagnetic and paramagnetic surfaces. By considering both single-crystal (100) surfaces and hypothetical free-standing (100) monolayers (ML's) of Ni, Rh, Pd, and Pt, we illustrate a broad range of interesting behaviors. The present emphasis on the magnetic properties of extended adsorbate systems represents a significant departure from previous calculations for NO chemisorption, which were either spin restricted,[9,10] or based on finite-cluster models.[11]

Recently, two of us examined the non-spin-polarized electronic structures of NO overlayers on Rh, Pd, and Pt (100) surfaces within the local-density approximation.[10] The interactions of NO with these particular metals is of great concern technologically, as one or more of these elements is usually essential for the catalytic abatement of NO$_x$ and other pollutants from motor vehicle exhaust.[12] The 4d elements Rh and Pd and the 5d element Pt are also interesting from a magnetic perspective, as they are all paramagnetic in bulk form, but tend to develop nonzero magnetic moments in systems with reduced coordination.[13–15] The present LSDA treatment of both (100) surfaces and free-standing (100) ML's is motivated by a desire to compare the magnetic properties of adsorbed NO in these two cases. The 3d element Ni is also included in this study to compare the behavior of NO on a bulk ferromagnet and to provide a closer connection to previous LSDA calculations.[2,13,16,17]

The all-electron pseudofunction method used in this work requires no empirical input and was designed specifically for problems in molecular chemisorption.[8] The LSDA is implemented in the form of the von Barth-Hedin exchange-correlation functional[7,18] Scalar-relativistic effects are included for all four metals, in accordance with most previous calculations for 4d and 5d elements.[13,15] Our chosen basis set for valence electrons consists of two s, six p, and five d orbitals centered on each metal atom and one s, three p, and five d orbitals centered on N and O. Calculated magnetic properties depend only weakly on the choice of muffin-tin radii used to construct these orbitals (2.00 bohrs for Ni, Rh, Pd, and Pt and 1.08 bohrs for N and O). All extended surfaces and chemisorbed systems are modeled as periodic supercells with vacuum spacings of 7.5 Å or greater. Metal atom positions are taken from truncated bulk coordinates, even for hypothetical free-standing ML's. Chemisorbed NO is modeled as half-monolayer ($\theta=0.5$), $c(2\times2)$ overlayers in either twofold bridge or atop sites on metal (100) surfaces. We assume the NO to be linearly coordinated through the N, with N-O, and metal-N spacings of 1.15 and 1.80 Å, respectively. Brillouin-zone integrations are performed using 15 $\mathbf{k}_\parallel$ points (12 for bridge sites) in the two-dimensional irreducible zones corresponding to the $c(2\times2)$ unit cells.

Magnetic moments calculated with this approach for clean metal slabs consisting of one and three (100) layers are listed in Table I. While a three-layer model is clearly a very crude representation of a semi-infinite surface, experience has shown that this thickness is generally sufficient to provide at least a qualitative description of some surface properties of close-packed metals such as magnetic moments,[9,13,19] although it is inadequate for describing others such as the dispersion of surface states.[20] The three-layer Ni results in Table I, for example, exhibit a similar enhancement of surface atom magnetic moments relative to interior atoms as seen in calculations for much thicker slabs.[13,20] This effect has been explained in terms of the band narrowing that occurs at a surface due to its reduced coordination.[20] The still

TABLE I. Magnetic moments (in μ_B) in muffin-tin spheres for one (ML) and three (3L) layer (100) metal slabs. Nearest-neighbor spacings are listed in parentheses. S and S-1 denote surface and subsurface atoms, respectively.

		Ni (1.76 Å)	Rh (1.90 Å)	Pd (1.95 Å)	Pt (1.96 Å)
ML		0.84	0.78	0.04	0.40
3L	S	0.73	0.00	0.00	0.03
	S-1	0.67	0.00	0.00	0.05

lower coordination in a free-standing ML further enhances the magnetic moment in Ni and gives rise to ferromagnetism in Rh and Pt (and very weakly in Pd) ML's, despite the absence of appreciable magnetic moments at the (100) surfaces of these bulk paramagnets.[21] All of the clean metal results in Table I are in reasonable quantitative agreement with previous LSDA calculations.[13,22] The general prediction that ferromagnetic ordering is possible in non-3d transition-metal systems with reduced coordination is also supported by recent experiments on Rh clusters[14] and on Ru ML's grown on graphite.[4]

A free NO molecule has an electronic structure similar to that of CO, but with one extra unpaired electron in its $2\pi^*$ orbital. Both molecules interact with transition-metal surfaces primarily through the hybridization of molecular 5σ levels with unoccupied d states (σ donation) and molecular $2\pi^*$ levels with occupied d states (π backbonding). The latter interaction dominates for NO on Ni, Rh, Pd, and Pt because of the high d-band fillings and close proximities of NO $2\pi^*$ and metal Fermi levels.[9,10] For relatively high coverages such as $\theta=0.5$, interactions between NO molecules are also significant.[10] These interactions cause the molecular levels to disperse, but they do not destroy the net spin on each molecule. At an NO-NO separation typical of the present overlayers, we find magnetic moments of 0.38 and $0.17\mu_B$ within the relatively small N and O muffin-tin spheres, respectively, and an additional $0.45\mu_B$ per molecule interstitially, for a hypothetical, free-standing NO ML with ferromagnetic ordering.

Of the two adsorption sites considered here, the present calculations always favor the bridge site, which allows for stronger π backbonding.[10] Experimental evidence is available for both types of bonding (see discussion in Ref. 10), with the bridge site clearly favored on Rh and Pd (100). Upon convergence to self-consistency, we find only negligible magnetic moments in all calculations for bridge-bonded NO overlayers on one- and three-layer (100) slabs of Rh, Pd, and Pt. Bridge-site adsorption on one- and three-layers Ni (100) slabs also causes a near total vanishing of N and O moments, and strongly suppresses the moments of Ni "surface" atoms. Converged moments for the three-layer Ni system are given in parentheses in Fig. 1. The predicted value of $0.06\mu_B$ for Ni atoms directly bonded to NO is similar to the value of $0.10\mu_B$ found for the analogous single-layer system. The magnetic moments of Ni atoms in the S-1 and S-2 layers of the three-layer system are also reduced by 27 and 10 %, respectively, by the presence of NO.

The projected majority- and minority-spin electron densities of states (DOS) for Ni_{S-1} and Ni_{S-2} in Fig. 1 are only slightly perturbed by the NO. The much narrower d-band region for Ni_{S-2} illustrates the reduced coordination effect discussed earlier, which results in an enhanced magnetic moment at a clean Ni surface.[20] The N+O and Ni_S DOS curves, on the other hand, show clearly the effects of π backbonding. For bridge-site adsorption, this interaction splits the NO $2\pi^*$ state into two distinct peaks: one centered at -2.8 eV and the other at 1.1 eV. The resulting two sets of hybridized states are primarily metal-N bonding and metal-N antibonding, respectively. The same NO $2\pi^*$-metal d interaction shifts the Ni_S DOS peak below that of a clean Ni surface (e.g., Ni_{S-2}) and effectively broadens the d band. The admixture of NO $2\pi^*$ orbitals lowers the effective exchange splitting of Ni_S d states and nearly eliminates the Ni_S magnetic moment. The involvement of the single NO $2\pi^*$ electron in a covalent bond with the metal[23] also eliminates the net spin density on the molecule.

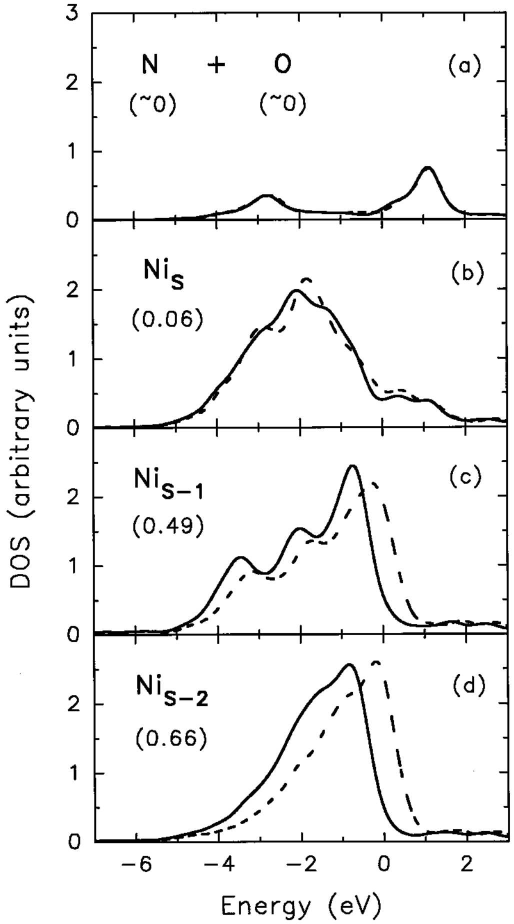

FIG. 1. Majority (solid) and minority (dashed) spin electron DOS (broadened by 0.2 eV) projected on orbitals associated with (a) N and O, and (b)–(d) Ni atoms in order of proximity to NO, for bridge-bonded NO overlayers on three-layer Ni (100) slab. The zero of energy is the Fermi level. Magnetic moments in parentheses.

The suppression of magnetic moments by bridge-bonded NO is not simply due to a filling of minority d states by NO $2\pi^*$ electrons. The total charge within muffin-tin spheres, in fact, increases slightly for N and O atoms because of π backbonding and differs by only 0.04 e^- between Ni_S and Ni_{S-2} atoms. Our previous non-spin-polarized calculations showed that the increased occupancies in antibonding NO

TABLE II. Magnetic moments (in μ_B) in muffin-tin spheres for $\theta=0.5$, $c(2\times2)$ overlayers of NO in atop sites on three-layer (100) metal slabs. S, S-1, and S-2 denote metal layers in order of proximity to NO. Asterisks denote atoms directly bonded to or aligned with NO.

		Ni	Rh	Pd	Pt
	O	0.00	0.00	0.02	0.00
	N	0.02	0.00	0.05	0.01
Metal	S^*	0.30	0.00	0.07	0.05
	S	0.74	0.00	0.25	0.21
	S-1	0.62	0.01	0.13	0.15
	$(S\text{-}2)^*$	0.63	0.02	0.07	0.11
	S-2	0.73	0.01	0.12	0.23

$2\pi^*$ states at bridge sites lead to roughly 10% increases in N-O bond lengths.[10] We have confirmed that the LSDA predicts a similar effect, but find that the associated changes in magnetic properties due to such an expansion are insignificant.

We next examine NO chemisorption in atop sites, which leads to a richer variety of magnetic behaviors. Converged moments for atop-bonded overlayers on three-layer (100) metal slabs are listed in Table II. On Ni, the N and O moments again disappear and the moment on the Ni atom directly bonded to NO is suppressed, albeit by a lesser amount than in the bridge-bonded case. The magnetic perturbation is more localized for atop-site chemisorption, although a 14% moment reduction occurs even in the S-2 layer on the Ni atom directly in line with the NO. The Pd and Pt systems in Table II exhibit chemisorption-induced ferromagnetism in the metal, with essentially no residual moments in the NO. The largest induced moments occur on the metal atoms not directly aligned with NO; the resulting spin distribution is thus qualitatively similar to that in the Ni system. The induced ferromagnetism results from slight increases in the already large densities of states at the Fermi levels in Pd and Pt (Ref. 24) upon NO chemisorption, which allow these systems to exceed the Stoner criterion for a magnetic instability; the moments are largest on those atoms which make the largest contributions to the states at the Fermi level. It would be interesting to extend the present calculations to thicker slabs to determine whether this effect is indeed characteristic of (100) surfaces or if it is restricted to relatively thin systems. Note that no magnetic moments remain or are induced in Rh, which has a much lower DOS at the Fermi level than Pd or Pt by virtue of its lower d-band filling.[24]

Rh and Pt (100) ML's with atop-bounded NO also exhibit negligible spin densities. These results, and the similar behavior predicted for bridge-bonded NO, are particularly noteworthy because of the sizable magnetic moments predicted for clean Rh and Pt ML's. Converged moments and associated DOS curves for atop-bonded NO on Ni and Pd (100) ML's are shown in Fig. 2. The predicted Ni moments are remarkably similar to those in the surface layer of the three-layer Ni system in Table II; the main difference is that the NO itself retains a net spin density on the ML. In both systems, atop-bonded NO shifts the DOS peak of the Ni atom directly bonded to NO to lower energy by about 2 eV,

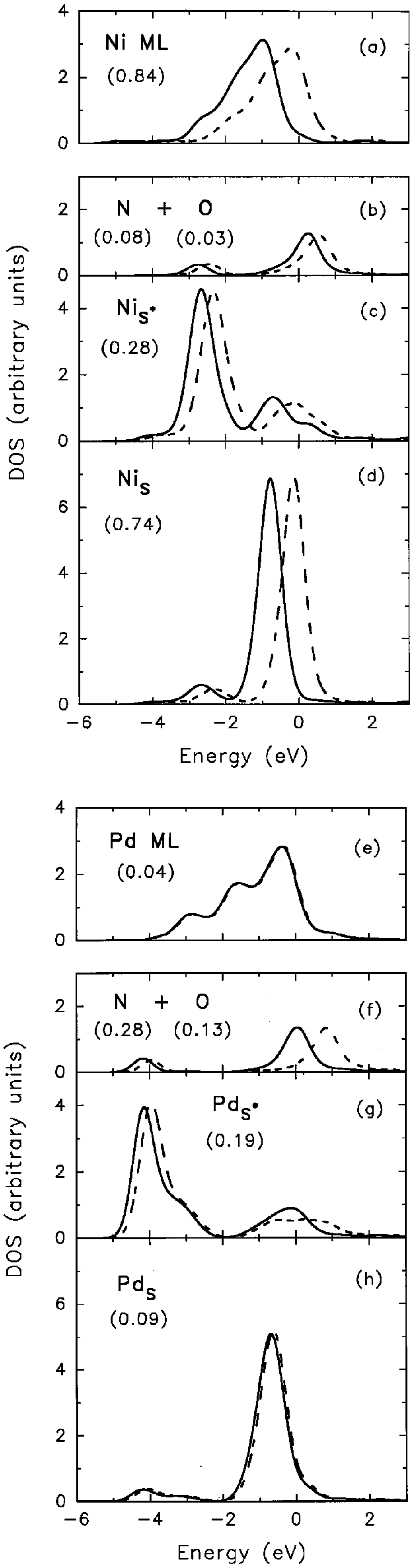

FIG. 2. Same as Fig. 1 but for (a) a clean Ni ML, (b)–(d) atop-bonded NO on a Ni ML, (e) a clean Pd ML, and (f)–(h) atop-bonded NO on a Pd ML.

as seen in Fig. 2(c). This reduces the bonding between Ni atoms, which causes the magnetic perturbation to remain relatively localized, and narrows the DOS at other sites, as in Fig. 2(d). A similar effect occurs in the Pd ML system in Figs. 2(f)–(h), although there the magnetic moments are in the opposite order compared to the Ni case: i.e., they are largest in the molecule, and smallest on the Pd atom not bonded to NO. The incomplete quenching of NO moments for atop-site adsorption is a consequence of the relatively weak π backbonding interaction in this geometry.[10] The magnetic moments for atop-bonded NO on a Pd ML, in fact, are only slightly reduced from their values in a free-standing NO ML, and the magnetic response of the Pd in this case is a consequence of its large magnetic susceptibility,[24] as in previous studies of ferromagnetic Fe, Co, and Ni overlayers on Pd.[13]

The above results suggest that NO chemisorption: (a) always strongly suppresses the magnetic moments of Ni atoms directly bonded to NO, (b) always completely quenches all magnetic moments on Rh, and (c) produces a wide variety of behaviors—from a complete quenching of magnetic moments, to induced ferromagnetism, to a retention of net NO spin density—on Pd and Pt, depending on the adsorption site and metal environment. The predicted behavior on Ni is qualitatively similar to that observed[1–3] or predicted[16,17] previously for other adsorbates, particularly CO. We have found, in fact, that analogous LSDA calculations for CO overlayers on Ni (100) lead to remarkably similar magnetic structures to those presented here. The present prediction that Rh ML moments are quenched by NO adsorption is also comparable to the recently observed quenching of Ru ML moments by CO adsorption.[4] It would be interesting to test experimentally whether a similar quenching occurs for NO adsorbed on Rh clusters.[14] The possible existence of a multiplet splitting in the N 1*s* core level x-ray photoemission spectrum[25] for NO on Rh (110) suggests that conclusion (b) above may not hold in general. A more definitive multiplet splitting in metastable deexcitation spectroscopy measurements[6] for NO on Pd and Pt (111) surfaces is most likely an example of the type of remnant NO spin polarization found here in Fig. 2(f). The tremendous variability in the predicted magnetic responses of Pd and Pt to NO chemisorption is a consequence of the close proximity of these metals to magnetic instabilities, which allow relatively small changes in geometries and associated densities of states to produce dramatic changes in behavior.[15]

Many other aspects of the chemisorption of paramagnetic molecules on ferromagnetic and paramagnetic metal surfaces remain to be investigated. Open issues include the effects of NO bending, the behavior on other surfaces and for other adsorption sites (e.g., hollow) and coverages, the possibility of more complicated magnetic orderings and the implications for the dynamics of adsorption and desorption. Sample calculations indicate that relatively gross properties, such as adsorption geometries and energetics, are not strongly affected by the breaking of spin symmetry. This, and the likely destruction of magnetic effects at elevated temperatures, imply that the interplay between adsorbate bonding and magnetism generally has little impact on catalysis.[12] A better understanding of this interplay, however, is of considerable importance to the magnetic recording industry[26] and might lead to novel sensor devices.

---

[1] C. S. Feigerle *et al.*, Phys. Rev. Lett. **56**, 2207 (1986).

[2] D. A. van Leeuwen *et al.*, Phys. Rev. Lett. **73**, 1432 (1994).

[3] P. W. Selwood, *Chemisorption and Magnetism* (Academic, New York, 1975).

[4] R. Pfandzetter, G. Steierl, and C. Rau, Phys. Rev. Lett. **74**, 3467 (1995).

[5] M. Farle, M. Zomack, and K. Baberschke, Surf. Sci. **160**, 205 (1985).

[6] W. Sesselmann *et al.*, Phys. Rev. Lett. **60**, 1434 (1988).

[7] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[8] R. V. Kasowski, M.-H. Tsai, T. N. Rhodin, and D. D. Chambliss, Phys. Rev. B **34**, 2656 (1986).

[9] T. R. Ward, R. Hoffman, and M. Shelef, Surf. Sci. **289**, 85 (1993).

[10] M.-H. Tsai and K. C. Hass, Phys. Rev. B **51**, 14 616 (1995).

[11] For example, C. W. Bauschlicher and P. S. Bagus, J. Chem. Phys. **80**, 944 (1984), and G. W. Smith and E. A. Carter, J. Phys. Chem. **95**, 2327 (1991).

[12] M. Shelef and G. W. Graham, Catal. Rev. Sci. Eng. **36**, 433 (1994).

[13] A. J. Freeman and R. Wu, J. Magn. Magn. Mater. **100**, 497 (1991), and references therein.

[14] A. J. Cox, J. G. Louderback, S. E. Apsel, and L. A. Bloomfield, Phys. Rev. B **49**, 12 295 (1994).

[15] S. Blügel, Phys. Rev. B **51**, 2025 (1995).

[16] M. Weinert and J. W. Davenport, Phys. Rev. Lett. **54**, 1547 (1985).

[17] F. Raatz and D. R. Salahub, Surf. Sci. **176**, 219 (1986).

[18] R. V. Kasowski, M.-H. Tsai, and J. D. Dow, Phys. Rev. B **41**, 8949 (1990).

[19] G. te Velde and E. J. Baerends, Chem. Phys. **177**, 399 (1993).

[20] E. Wimmer, A. J. Freeman, and H. Krakauer, Phys. Rev. B **30**, 3113 (1984).

[21] M. Weinert, S. Blügel, and P. D. Johnson, Phys. Rev. Lett. **71**, 4097 (1993).

[22] Additional test calculations for ML's with expanded lattice constants (such as would be present on nonmagnetic supports) compare well with previous results cited in Refs. 4 and 13.

[23] M. E. Bartram, B. E. Koel, and E. A. Carter, Surf. Sci. **219**, 480 (1989).

[24] O. K. Anderson, Phys. Rev. B **2**, 883 (1970).

[25] R. J. Baird, R. C. Ku, and P. Wynblatt, Surf. Sci. **97**, 346 (1980).

[26] L. M. Falicov *et al.*, J. Mater. Res. **5**, 1299 (1990).