PHYSICAL REVIEW B VOLUME 59, NUMBER 6 1 FEBRUARY 1999-II

Tight-binding study of the CO chemisorption effect on cobalt magnetization

Štěpán Pick
Jaroslav Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3,
CZ-182 23 Prague 8, Czech Republic

Hugues Dreyssé
Institut de Physique et Chimie des Matériaux de Strasbourg, UMR CNRS 46, 23 rue du Loess, Boîte Postale 20 CR,
F-67037 Strasbourg Cedex, France

(Received 15 July 1998)

By using a semiempirical self-consistent tight-binding scheme we study the effect of O and CO chemisorption on the Co(0001) surface magnetization. Similar calculations are performed for the Co_{13} and Co_{55} clusters of high symmetry. The CO molecule in the atop position, but not in the bridge geometry, is effective in local magnetization quenching. In clusters magnetic phase transitions are observed as the Co-CO separation varies. When the separation is more than about 1.8 Å, the Co magnetization remains strong. The character of phase transitions conforms to the formal predictions based on the Landau theory. [S0163-1829(99)10705-7]

I. INTRODUCTION

Films and surfaces of ferromagnetic transition metals (TM's) have an outstanding role in the recording media development. Recently it has become clear that an effect with promising application in the magnetic information storage—the giant magnetoresistance—is advantageously realized in granular systems. Particularly, cobalt clusters immersed into a noble-metal matrix are intensively studied.[1,2] We mention also systematic studies of cobalt nanoparticles in colloids.[3,4] Several authors find indication of ferromagnetism quenching in such systems.[2,3,5] This is an unexpected result since, generally, there is a abundant evidence that in Co clusters the magnetization is quite strong as documented, e.g., by the experimental[6–8] and theoretical[9,10] studies. The authors of experiments[3,5] stress the oxidation of Co clusters as a likely explanation. Actually, a possible surface-oxide formation has been reported for Co clusters[1] and the (0001) surface,[11] respectively. In Ref. 2 the contamination by oxygen is very low and a specific kind of interaction that hinders parallel arrangement of the cluster magnetic moments is proposed. Influence of CO adsorption on Co clusters has been also studied experimentally[4] and the magnetization quenching seems to be established. There are also other reasons why CO adsorption on Co surfaces deserves attention. First, it has been found recently that minute doses of CO induce a magnetic anisotropy switch in Co films.[12] Second, importance of most differing Co systems in catalysis is recognized.

It is useful to remind the reader of further results on the chemisorption on ferromagnetic surfaces, films, and clusters. For the strong ferromagnet iron, the oxygen chemisorption leads to a slight enhancement of magnetization.[13–15] It is likely[16] that the enhancement is due to the oxygen-induced surface expansion.[13–15] Only when oxygen penetrates into the metal and/or an oxide is formed, the situation changes.[17] However, it is not clear whether magnetization quenching or an antiferromagnetic arrangement driven in oxides by superexchange[18] takes place. The influence of sulfur on surface magnetization is more serious but it is still far from being drastic.[19,20] The recent photoemission study[21] shows that the disordered oxygen on Co(0001) does not remove the exchange splitting of cobalt *d*-electron states, and the asymmetry of the magnetic circular dichroism spectra is only partly reduced.

For the comparatively weak ferromagnet nickel, the oxygen[22] and hydrogen[23] seriously affect the magnetization. The recent calculations[24] show, in accord with experiments, that CO kills the magnetization at the surface of Ni clusters. Quite recently, a similar behavior has also been observed for Co clusters on sapphire.[25]

The tight-binding model of the hypothetical magnetic V(001) surface concludes[16] that the effect of oxygen is strong (weak) if the free surface magnetization is weak (strong).

For CO on the Co(0001) surface several experiments exist[26,27] that, however, do not give information on the surface magnetization. However, the spin-polarized photoemission spectra[28] resolve no splitting of the CO 5σ peak and this is a strong indication of a substantial local magnetization quenching. Indeed, the position of the 5σ level is strongly influenced by the interaction with the neighboring metal atom(s). If the effective atomic *d*-electron levels on these atoms were essentially different for majority- and minority-spin states, respectively, there should be a spin dependent splitting of the 5σ level even without spin-polarization of the molecule.

That is why we believe that it is of interest to extend our semiempirical calculations of oxygen[16] and CO (Ref. 29) adsorption on magnetic surfaces to the Co(0001) surface and cobalt clusters, respectively. Of course, it is not the aim of the present semiquantitative study to present fully realistic results. First, the adsorption geometries are not well known (see below) and we are forced to accept a guess. Second, the TM carbonyls adopt complicated structures with a huge number of CO's.[24,30] Our purpose is rather to analyze a number of simple ''generic'' situations and to try to understand the general trends.

For oxygen the situation appears to be simple and the results resemble those known for iron, but for CO the results are more involved. Some preliminary results have been published in Ref. 31.

II. MODEL

In our calculations we employ semiempirical tight-binding Hamiltonians treated self-consistently within the recursion method scheme. The real-space recursion method[32] provides a versatile tool to obtain the local densities of electronic states even for systems without translational symmetry. For Co systems without adsorbates we use the s-d electron Hamiltonian in which the Coulomb integrals (diagonal Hamiltonian matrix elements) are adjusted to obey the local charge neutrality assumption. The difference between the spin-up and spin-down d-electron Coulomb integrals (exchange splitting) at the site i is calculated from the self-consistent condition $\epsilon_i^{\downarrow}-\epsilon_i^{\uparrow}=Jm_i$. Above, m_i is the local magnetization and J is the exchange integral that is supposed to be site independent. The parametrization is fully described in Ref. 29 for Co(0001); for Co clusters we omit the crystal-field splitting that has been introduced[29] to fit better details the Co bulk band structure. Our previous experience as well as some numerical tests give us hope, however, that the quantities we are interested in are not sensitive to such a simplification.

To study the chemisorption, the O $(2p)$ orbitals[16,33] or the CO 5σ and $2\pi^*$ orbitals,[34,35] respectively, are included. The (nearest-neighbor) O-Co and C-Co hopping integrals are derived from the Slater-Koster parameters of Harrison;[36] the $d^{-7/2}$ distance scaling is understood.[36] Only the interaction of adsorbate electrons with d electrons of the metal is considered. To evaluate in the described manner the hopping integrals between the CO and Co $(3d)$ electrons, respectively, the molecular 5σ and $2\pi^*$ states must be decomposed into atomic orbitals.[35] This information is taken from Ref. 37.

In the presence of chemisorption we allow a transfer of charge between the Co d electrons and the adsorbate. The main idea is to control the metal d-electron and adsorbate Coulomb integrals by the equation

$$\epsilon_i=\epsilon_i^0+U_i(n_i-n_i^0). \tag{1}$$

Here, U_i is the metal d-electron or adsorbate Coulomb parameter, n_i is the electron occupation number, and the superscript ‘‘0’’ refers to the state before chemisorption. The use of only one parameter U_i per site i supposes averaging over the screened atomic multiplets lying close in energy, similarly as in the local density methods. Such an assumption is well justified, e.g., for typical metallic sytems. In our calculations, we allow the orbital self-interaction for cobalt $3d$ and oxygen $2p$ states. A modification of Eq. (1) with the orbital self-interaction excluded[33,38] is a nontrivial problem since it turns, generally speaking, to depend on the choice of the orbital basis.[38] For CO there is a natural basis choice (5σ and $2\pi^*$ states) and we prefer to modify the Eq. (1) to exclude the orbital self-interaction (cf. Ref. 34) but we average the resulting values over the two spin orientations. The spin dependence of cobalt Coulomb integrals is controlled by the parameter J introduced above. The correct model must yield a globally charged neutral solution and for semi-infinite systems with the Fermi level E_F fixed this is not ensured by Eq. (1). We use a ‘‘charge renormalization’’ method that tends to reduce the charge transfer predicted by Eq. (1). The method is described into detail in Ref. 16 for oxygen and in Ref. 35 for the CO adsorption. For clusters, the global charge neutrality can be obtained either by the same ‘‘charge renormalization’’ as for infinite systems, or adjusting properly E_F. We have found that the two methods lead to very similar conclusions and use the second possibility (E_F adjusting). The position of the adsorbate Coulomb integrals ϵ^0 with respect to E_F can be deduced from the experimental work function for Co(0001) (Refs. 29 and 34) and we suppose the same position with respect to the free cluster E_F. This is a simplifying assumption but our experience shows that the global charge neutrality condition has strong tendency to suppress in final results the uncertainty associated with the adsorbate ϵ^0’s.

Together with the semi-infinite Co(0001) we consider several clusters. The geometry of Co clusters in the noble-metal matrix is not known with certainty and speculations about a structure with a bcc core exist;[5,3] another interpretation of experiments suggests icosahedral motives.[39] We consider symmetric fcc Co_n $(n=13$ or 55) and icosahedral 13-atom clusters. In fcc clusters the nearest-neighbor separation is taken as that in the bulk Co (2.5 Å). We have checked for several geometries that the results do not change drastically when the distance is shortened by 5%. For icosahedral clusters the Co-Co distance d_{ss} between the surface nearest neighbors is by 5% longer than the surface-central atom separation d_{sc}. We study the geometry with $d_{sc}=2.5$ Å and also the ‘‘compressed’’ icosahedral clusters (denoted as ico* in the next section) with $d_{ss}=2.5$ Å.

We calculate the magnetization when a single O or an (1×1) oxygen overlayer is put at the threefold fcc-like site above Co(0001), and an isolated O adatom at the threefold site on the fcc Co_{13} cluster. The Co-O separation of 2.0 Å is consistent with the distance in the bulk CoO as well as with a guess based on typical atomic radii in chemisorption systems.[13–15,40] For CO adsorption at Co(0001) the atop site is first populated with the subsequent adsorption in bridge position[26,27] and the same positions are found for CO on Co clusters (carbonyls).[41] The molecule adsorbs by the carbon end. The calculations for paramagnetic Co clusters[42] arrive at a large Co-CO separation of 1.91 Å (atop) and 2.05 Å (bridge). The experiments on clusters[5] give also indication of a large Co-CO separation; the whole matter is, however, rather complicated.[39] For the above distances our calculations find but a weak Co-CO interaction with no effect on Co magnetization and with the CO 5σ level position contradicting the experiment.[26–28] Actually, we believe that the choice of 1.75 Å for the atop and 1.90 Å for the bridge site, respec-

TABLE I. Magnetic moments (in μ_B) at the free (first column) or adsorbate-covered Co(0001) surface. m_s and m_a refer to the cobalt surface atom(s) at the adsorbate, and to the adsorbate, respectively.

Adsorbate		O	O(1×1)	CO (atop)	CO (bridge)
m_s	1.70	1.73	1.43	0.48	1.61
m_a		0.36	0.08	−0.03	0.10

TABLE II. Local magnetic moments m (in μ_B) at the free Co clusters (first three rows) or at clusters with a single O at the threefold site, or CO at atop site. fcc and icosahedral (ico) geometries are considered; see Sec. II for definition of the compressed ico* cluster. The subscripts s,c refer to the surface or central Co atom, and a to the adsorbate. The superscripts 0–4 label the surface Co atoms according to their distance from the adsorbate; 0 denotes the adsorbate nearest neighbor(s). The numbers in parentheses, $(m;n)$ or (m), mean the number of Co atoms of the given kind (m) and their coordination (n), respectively. The paramagnetic solution in CO_{12}/Co_{13} (last line) is found for all the three fcc, ico, and ico* clusters.

System	m_s^0	m_s^1	m_s^2	m_s^3	m_s^4	m_c	m_a
fcc Co_{13}	1.85 (12;7)					1.61 (1;12)	
ico Co_{13}	1.83 (12;6)					1.65 (1;12)	
ico*Co_{13}	1.74 (12;6)					1.63 (1;12)	
O/fcc Co_{13}	1.77 (3)	1.74 (6)	1.74 (3)			1.68	0.06
CO/fcc Co_{13}	−0.13 (1)	1.76 (4)	1.80 (2)	1.76 (4)	1.80 (1)	1.54	−0.08
CO/ico Co_{13}	−0.11 (1)	1.81 (5)	1.86 (5)	1.93 (1)		1.55	−0.03
CO/ico*Co_{13}	−0.02 (1)	1.79 (5)	1.82 (5)	1.89 (1)		1.50	−0.04
CO_{12}/Co_{13}	0.00 (12)					0.00 (1)	0.00

tively, is more likely. (1) The CO chemisorption on Co(0001) and Pt(111), respectively, are similar[43] and the above guess is consistent with the Pt-CO separation[40,44] when the difference between the metallic radii of Pt and Co is taken into account. (2) Our guess agrees with the experiment on Co carbonyls.[41] (3) We get the correct behavior of the 5σ level (see below).

In our calculations, the Coulomb integrals and exchange-splitting changes induced by chemisorption were recalculated on several adsorbate Co neighbors as follows: on first- and second-nearest surface neighbors for isolated O and CO on Co(0001) (for CO in the atop position, also its first subsurface neighbors were included) and for O(1×1), on all Co atoms in the first three (0001) atomic planes. For more distant atoms, the values from adsorbate free calculations were employed. For clusters, the self-consistent calculations were performed for all atoms.

III. RESULTS AND DISCUSSION

Let us mention first the results for the adsorbate-free systems. Below, we show the magnetization of Co atoms due to d electrons only. For s electrons we always get a negative magnetization of several hundredths of μ_B supposing that the atom remains well magnetized. This is in semiquantitative agreement with first-principles calculations,[45] but omission of p electrons in our model limits the accuracy. For Co(0001) we get the surface (bulk) magnetization 1.70 (1.68) μ_B. For clusters the data presented below show a further surface magnetic moment enhancement. The values remain nevertheless somewhat lower than expected,[6,9] apparently because of the use of parameters fitted to the bulk properties.[29]

For the convenience of the reader we show in Fig. 2 geometry of the Co_{13} clusters with different adsorbate geometries considered below. We find that the oxygen adsorption changes only moderately the Co(0001) magnetization (Table I) and the same is true for the fcc Co_{13} cluster. The finding is consistent with the measurement for oxygen on the Co(0001) surface.[21] The small enhancement of the magnetization on some Co atoms induced by the chemisorption of O (or of CO, see Tables I and II) results probably from the fact that the minority-spin electrons with a higher local density of states (LDOS) at E_F donate more charge to the adsorbate. The magnetization of oxygen is always parallel (ferromag-

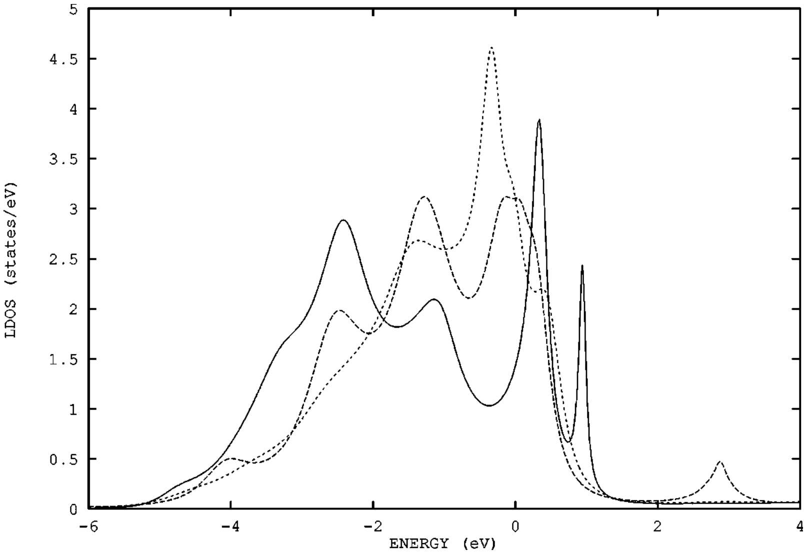

FIG. 1. Local density of electronic states at the free Co(0001) surface atom (short-dashed line) and at a Co surface atom interacting with CO in atop (full line) and bridge (long-dashed) position, respectively. The paramagnetic Co crystal is considered. The Fermi level lies at the energy zero. The peaks at low energy originating from the interaction with CO(5σ) states are not shown.

TABLE III. Local magnetic moments m (in μ_B) at the free or CO-covered fcc Co_{55} cluster. The subscripts 0–4 label the Co atoms according to their distance from the cluster center: ''0'' denotes the outermost and ''4'' the central atom, respectively. m_a is the CO magnetic moment. The meaning of data in parentheses $(m;n)$ or (m) is the same as in Table II.

System	m_0	m_1	m_2	m_3	m_4	m_a
fcc Co_{55}	1.82 (12;5)	1.75 (24;5)	1.75 (6;8)	1.65 (12;12)	1.76 (1;12)	
CO_{12}/fcc Co_{55}	−0.05	1.73	1.79	1.57	1.73	−0.05

netic), but it is rather suppressed at the cluster as a result of a higher ionicity than at Co(0001). The latter effect can be overestimated in our model since in the semi-infinite metal and clusters, respectively, a different number of atoms is allowed to participate in the charge transfer (see the preceding section).

For the atop-adsorbed CO we find the 5σ peak with a slight spin-splitting of 0.1 eV at 7.7 and 7.8 eV below E_F, in satisfactory agreement with the photoemission spectra.[26–28] However, the far most interesting finding (Table I) is the difference between the CO atop and bridge adsorption, respectively. It is only in the former case that the magnetization at the Co atom next to CO gets quenched drastically. (We do not show changes at more distant Co atoms since they are unessential.) To understand the nature of the effect we present in Fig. 1 the LDOS at the *paramagnetic* Co(0001) surface atom before and after its interaction with CO in the atop or bridge site, respectively. LDOS at E_F is perturbed quite differently for the two adsorption sites, which together with the Stoner criterion explains the situation. We have analyzed the Co-CO interaction and we think that it is mainly the high symmetry that makes the LDOS split substantially more for the atop adsorption. For the Co-CO($2\pi^*$) interaction at least, the purely π bond in the atop geometry becomes a mixture of π and σ interactions that strongly compensates the larger separation in the bridge geometry. Single CO in atop position, with the CO axis oriented in the radial direction, leads to a large magnetization lowering at clusters as well, with an antiferromagnetic coupling to the rest of cluster (Table II). We made also calculations for CO_{12}/Co_{13} systems for the fcc, ico, and ico* clusters. In these systems there is an atop-adsorbed CO at each ''surface'' Co atom. These systems turn to be nonmagnetic. The results for the CO_{12}/fcc CO_{55} system, with CO molecules adsorbed on the 12 outermost Co atoms are displayed in Table III. The ''surface'' Co atoms are almost nonmagnetic with an antiferromagnetic coupling to the cluster core. The ferromagnetic core is but slightly perturbed. The magnetic moment of the CO molecule is small in all cases (Tables I–III). The finding that for the completely covered surface (CO_{12}) the small Co_{13} clusters become paramagnetic whereas in the Co_{55} cluster the core remains virtually nonperturbed conforms to the conclusions on Ni clusters.[24] The magnetization quenching by CO at the surface of supported Co slusters has been observed recently[25] as well as some kind of magnetization suppression for Co clusters in colloids.[4] We calculated also hypothetical CO_2/fcc Co_{13} with a pair of CO molecules forming a wide ''V'' (or rather ''L'' since the two CO axes are mutually perpendicular, Fig. 2) adsorbed at a common Co atom. The magnetic moment at the latter Co atom is $0.31\mu_B$, which is somewhat more than for a single CO adsorbate (Table II). This corroborates our idea that the high symmetry of the upright atop chemisorption geometry is important.

An interesting property that we find for all CO/Co clusters is a phase transition as the Co-CO distance varies. The critical distance is always $d_c = 1.78 - 1.80$ Å. There are two situations. (1) ''First-order'' transition occurs for single CO on all Co_{13} clusters as well as for the CO_{12}/fcc Co_{55} system. Two solutions exist in the neighborhood of d_c, one with the locally suppressed magnetization (Tables II and III), and another one with the Co magnetic moments only slightly perturbed (~ 1.5–$1.6\mu_B$ on the Co neighbor of CO). The electronic energy evaluation shows that the former (latter) solution is less stable for Co-CO distances above (below) d_c. (2) ''Second-order'' transition is found for the CO_{12}/Co_{13} clusters. Below d_c, there is only paramagnetic solution. For larger separations, the magnetization is again only weakly reduced. Actually, such a behavior is in accord with nonrigorous arguments based on the Landau (mean-field) theory of phase transitions.[46] To see it, let us in case (1) denote by m the local magnetic moment at the atom(s) perturbed by CO and by M the magnetization at more distant atoms. Let us also expand the system energy as

$$E(m,M,d) = a(M,d)m + b(M,d)m^2 + c(M,d)m^3 + \cdots. \tag{2}$$

Since $M \neq 0$ near d_c, both a and c in Eq. (2) are nonzero. The presence of odd powers in the energy expansion leads to the first-order-like situation described above: The energy (2) can have two minima at $m_{1,2}, m_1 \neq -m_2$, and the difference

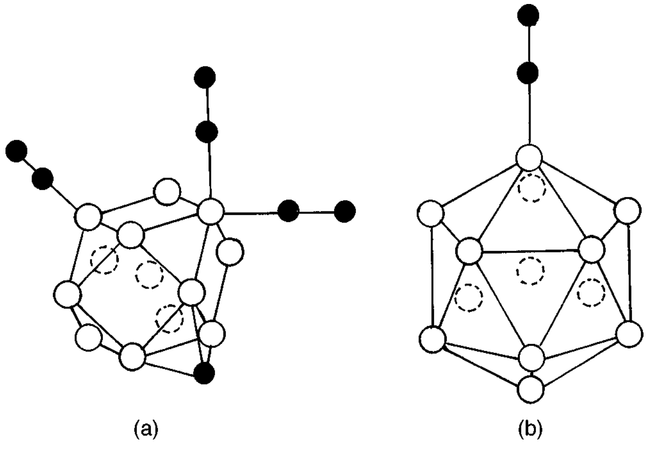

FIG. 2. The fcc (a) and icosahedral (b) Co_{13} clusters with adsorbates in different geometries as discussed in the text. Co atoms are represented by open circles whereas black circles correspond to O in the threefold position (single circle) or to CO adsorbed atop (pair of circles), respectively.

$E(m_1)-E(m_2)$ changes its sign at d_c. In case (2) all the moments tend to zero as one approaches d_c from above. Let them be proportional to m. Due to the symmetry $m\rightarrow -m$ one has

$$E(m,d)=a(d)m^2+b(d)m^4+\cdots. \tag{3}$$

Above d_c one has $m_1=-m_2\neq 0$ for the two energy minima and only the paramagnetic solution below d_c.[46] Our calculation has only approximate character because of its semiempirical character as well as because of perhaps not fully realistic geometry. It is nevertheless remarkable that the physics starts to be interesting just as we are close to the Co-CO distance 1.75 Å introduced above on different grounds. We have found similar bifurcation neither for the oxygen adsorption, nor for CO on Co(0001).

IV. CONCLUSIONS

We have studied chemisorption of oxygen and carbon monoxide, respectively, on a Co(0001) surface and on several Co clusters. Oxygen does not affect the Co magnetization essentially. Still, a magnetization weakening can be expected if the oxygen penetrates below the surface, or if an oxide is formed. However, CO turns out to be a good *local* magnetization killer when it adsorbs in the atop position. In clusters, the small quenched magnetic moments show tendency to antiferromagnetic coupling with the rest of the cluster. As the Co-CO distance varies we encounter in clusters magnetic phase transitions that agree formally with predictions of the Landau theory of phase transitions.

ACKNOWLEDGMENTS

We are indebted to Dr. Jean Marc Broto, Dr. Marc Respaud, and Dr. Marc Verelst for useful information on their experiments. The study has been facilitated by the common Project Scheme of Center National de la Recherche Scientifique and Academy of Sciences of the Czech Republic. Š.P. acknowledges support by the Grant agency of the Czech Republic, No. 203/96/0951, and the kind hospitality of the Institute de Physique et Chimie des Matériaux de Strasbourg.

---

[1] S. Sako, K. Oshima, M. Sakai, and S. Bandow, Surf. Rev. Lett. **3**, 109 (1996).

[2] D.A. Eastham, Y. Quing, T.H. Maddock, J. Kraft, J.P. Schille, G.S. Thompson, and H. Haberland, J. Phys.: Condens. Matter **9**, L497 (1997).

[3] T. Ould-Ely, C. Amiens, B. Chaudret, E. Snoeck, M. Verelst, P. Lecante, J.-M. Broto, and A. Fert (unpublished).

[4] M. Respaud, J.M. Broto, H. Rakoto, A.R. Fert, L. Thomas, B. Barbara, M. Verelst, E. Snoeck, P. Lecante, A. Mosset, J. Osuna, T. Ould Ely, C. Amiens, and B. Chaudret, Phys. Rev. B **57**, 2925 (1998).

[5] F. Parent, Ph.D. thesis, Université de Paris-Sud, 1996.

[6] J.P. Bucher, D.C. Douglass, and L.A. Bloomfield, Phys. Rev. Lett. **66**, 3052 (1996).

[7] J.M.L. Billas, A. Châtelain, and W.A. de Heer, Surf. Rev. Lett. **3**, 429 (1996).

[8] T. Thomson, P.C. Riedi, S. Sankar, and A. E. Berkowitz, J. Appl. Phys. **81**, 5549 (1997).

[9] Z.Q. Li and B.L. Gu, Phys. Rev. B **13** 611, (1993).

[10] Xiao Chuanyun, Yan Jinlong, Deng Kaiming, and Wang Kelin, Phys. Rev. B **55**, 3677 (1997).

[11] M. Getzlaff, J. Bansmann, and G. Schönhense, J. Electron Spectrosc. Relat. Phenom. **77**, 197 (1996).

[12] J.A.C. Bland, S. Hope, M. Tselepi, and B. Choi, J. Phys. D **31**, 622 (1998); S. Hope, E. Gu, B. Choi, and J.A.C. Bland, Phys. Rev. Lett. **80**, 1750 (1998); S. Hope, E. Gu, M. Tselepi, M.E. Buckley, and J.A.C. Bland, Phys. Rev. B **57**, 7454 (1998).

[13] Hong Huang and J. Hermanson, Phys. Rev. B **32**, 6312 (1985).

[14] S.R. Chubb and W.E. Pickett, Phys. Rev. Lett. **58**, 1248 (1987).

[15] R. Wu and A.J. Freeman, Phys. Rev. B **45**, 7532 (1992).

[16] Š. Pick and H. Dreyssé, Surf. Sci. **394**, 192 (1997).

[17] P. Ferro, R. Moroni, M. Salvietti, M. Canepa, and L. Mattera, Surf. Sci. **407**, 212 (1998).

[18] P.W. Anderson, Phys. Rev. **115**, 2 (1959).

[19] S.R. Chubb and W.E. Pickett, Phys. Rev. B **38**, 10 227 (1988).

[20] G. Rossi, G. Panaccione, and F. Sirotti, Phys. Rev. B **54**, 4080 (1996).

[21] J. Bansmann, L. Lu, and M. Getzlaff, Surf. Sci. **402-404**, 371 (1998).

[22] F. May, M. Tischer, D. Arvanitis, J. Hunter Dunn, H. Henneken, H. Wende, R. Chauvistré, N. Mørtensson, and K. Baberschke, Phys. Rev. B **53**, 1076 (1996).

[23] G. Allan, Surf. Sci. Rep. **1**, 121 (1981), and references given therein.

[24] G. Pacchioni and N. Rösch, Acc. Chem. Res. **28**, 390 (1995), and references given therein.

[25] T. Hill, M. Mozaffari-Afshar, J. Schmidt, T. Risse, S. Stempel, M. Heemeier, and H.-J. Freund, Chem. Phys. Lett. **292**, 524 (1998).

[26] H. Papp, Surf. Sci. **129**, 205 (1983).

[27] F. Greuter, D. Heskett, E.W. Plummer, and H.-J. Freund, Phys. Rev. B **27**, 7117 (1985).

[28] M. Getzlaff, J. Bansmann, and G. Schönhense, J. Chem. Phys. **103**, 6691 (1995).

[29] Š. Pick, Phys. Rev. B **57**, 1942 (1998).

[30] J.E. Huheey, *Inorganic Chemistry*, 3rd ed. (Harper and Row, New York, 1983).

[31] Š. Pick and H. Dreyssé, J. Magn. Magn. Mater. (to be published).

[32] R. Haydock, V. Heine, and M.J. Kelly, J. Phys. C **8**, 2591 (1975).

[33] C.M. Varma and A.J. Wilson, Phys. Rev. B **22**, 3795 (1980); A.J. Wilson and C.M. Varma, *ibid.* **22**, 3805 (1980).

[34] W. Andreoni and C.M. Varma, Phys. Rev. B **23**, 437 (1981).

[35] Š. Pick, J. Phys.: Condens. Matter **7**, 7729 (1995).

[36] W.A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[37] B.J. Ransil, Rev. Mod. Phys. **32**, 245 (1969).

[38] M. Arai and T. Fujiwara, Phys. Rev. B **51**, 1477 (1995).

[39] M. Verelst (private communication).

[40] M. A. Van Hove, S.-W. Wang, D.F. Ogletree, and G. Somorjai, Adv. Quantum Chem. **20**, 1 (1989).

[41] V. Albano, P. Chini, and V. Scattariw, J. Organomet. Chem. **15**,

423 (1968); V.G. Albano, P.L. Bellon, P. Chini, and V. Scatturin, *ibid.* **16**, 461 (1969).

[42] M.C. Zonnevylle, J.J.C. Geerlings, and R.A. van Santen, J. Catal. **148**, 412 (1994).

[43] S.-i. Ishi, Y. Ohno, and B. Viswanathan, Surf. Sci. **161**, 349 (1985).

[44] G. Pacchioni, S.-C. Chung, S. Krüger, and N. Rösch, Surf. Sci. **392**, 173 (1997); P.H.T. Philipsen, E. van Lenthe, J.G. Snijders, and E.J. Baerends, Phys. Rev. B **56**, 13 556 (1997).

[45] O. Eriksson, G.W. Fernando, R.C. Albers, and A.M. Boring, Solid State Commun. **78**, 801 (1991).

[46] L.D. Landau and E.M. Lifshitz, *Statistical Physics, Part I*, 3rd ed. (completed by E.M. Lifshitz and L.P. Pitaevskii) (Pergamon, New York, 1980), translated from Russian (Nauka, Moscow, 1978).