Reversible enhancement of the magnetism of ultrathin Co films by H adsorption

S. Gallego, N. Sanchez, S. Martin, and M. C. Muñoz

Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, 28049 Madrid, Spain

L. Szunyogh

Department of Theoretical Physics, Budapest University of Technology and Economics, Budafoki út 8., H-1111 Budapest, Hungary

By means of *ab initio* calculations, we have investigated the effect of H adsorption on the structural, electronic, and magnetic properties of ultrathin Co films on Ru(0001). Our calculations predict that H occupies hollow sites preserving the two-dimensional threefold symmetry. The formation of a complete H overlayer leads to a very stable surface with strong H-Co bonds. H tends to suppress surface features, in particular, the enhancement of the magnetic moments of the bare film. The H-induced effects are mostly confined to the Co atoms bonded to H, independent of the H coverage or of the thickness and the structure of the Co film. However, for partial H coverages a significant increase occurs in the magnetic moment for the surface Co atoms not bonded to H, leading to a net enhancement of surface magnetism.

I. INTRODUCTION

Hydrogen is an ubiquitous element, present even in ultrahigh-vacuum chambers, although very difficult to detect. It shows a large sticking probability in most transition-metal surfaces,[1] among them Co. Adsorption of H on transition metals was intensively studied in the past decades, mainly motivated by the understanding of the action of residual gases in catalytic and embrittlement processes.[2,3] Particularly for Co, much less attention has been paid to the influence of H on the magnetic properties, though it is known to have a remarkable effect. For example, the adsorption of H_2 molecules on the surface of magnetic transition metals usually produces a reduction in surface magnetism,[4,5] although a much rich physical scenario can be obtained at low-dimensional structures such as nanowires[6] or small clusters.[7] In addition, H coverage shifts the critical thickness for the spin reorientation transition (SRT) of Ni films,[8–10] and alters the magnetic anisotropy of Fe and Co nanoclusters.[7] Also in different V heterostructures it has been demonstrated that a reversible manipulation of the magnetic properties can be achieved upon loading the V layers with H.[11–13]

Previous experimental results characterizing the structure and energetics of H adsorption on different Co surfaces and nanostructures with two-dimensional (2D) threefold symmetry, as Co(0001) (Ref. 14) or Co nanoislands on Cu(111),[15] indicate that H prefers adsorption sites preserving the symmetry of the 2D lattice. This is in agreement with *ab initio* calculations of the hcp Co(0001) termination.[16] Even for Co($10\bar{1}0$) the formation of superstructures leading to adsorption sites of threefold symmetry has been reported.[17] The evaporation of molecular H_2 on different Co surfaces results in the dissociative chemisorption of H atoms up to a monolayer (ML) completion.[15] For higher doses, molecular H_2 physisorption occurs. The desorption of H from Co nanoislands on Cu(111) takes place locally and leaves the Co surface as it was prior the H evaporation, in contrast to the substrate exposed areas.[15] This surface character of the H-Co interaction is also supported by total-energy calculations,

which show a negligible weight of the H-induced states even in subsurface Co atoms.[16,18] In addition, no dependence of the binding energy on the H coverage is obtained.[16] Moreover, H subsurface sites are highly unstable, indicating a low probability for H diffusion to the bulk, which is also confirmed experimentally.[19]

As compared to other transition-metal surfaces, there are only a few studies of the influence of H on the electronic and magnetic properties of Co surfaces and thin films. Spectroscopic measurements indicate a quenching of the *sp*-like surface states and a shift of the *d* surface states downward in energy upon H adsorption.[20,21] Moreover, the Co electronic properties can be tuned individually controlling the amount of adsorbed H.[22] The calculated density of states (DOS) also indicates that H states appear below the *d* valence band (VB).[16] When spin-polarization is included, it can be shown that this results in the quenching of the surface-induced enhancement of the Co spin moment, at least for 1 ML of H coverage.[18,23]

Recently, we studied the magnetic properties of ultrathin Co films grown on Ru(0001).[24] This is a unique system showing a double SRT linked to the completion of Co atomic layers. The SRT is intimately related to the structural distortion of the ultrathin Co film. Both Co and Ru are hcp metals but with very different lattice parameters: 2.51 Å and 2.71 Å, respectively. While 1 ML of Co grows epitaxially, the second layer starts compressing toward the Co lattice, leading to an intermediate 2D lattice parameter of 2.6 Å. In this work we study the influence of H adsorption on the structural, electronic, and magnetic properties of these ultrathin Co/Ru(0001) films, with special emphasis on the 2 ML thick ones which show perpendicular magnetic anisotropy. The study of the magnetic anisotropy will be the subject of a forthcoming paper. Our results indicate that H bonds strongly to the surface and tends to form a complete overlayer leading to a very stable surface system. Partial H coverage, although thermodynamically stable, presents slightly smaller energies of adsorption. As we will show while 1 ML of H quenches the surface magnetism, lower H coverage may enhance it.
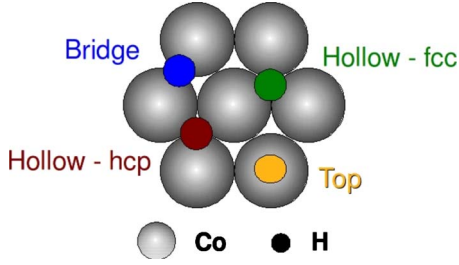
FIG. 1. (Color online) High symmetry sites for the adsorption of H on hcp Co.

This can be a crucial factor regarding the role of residual H in the measured magnetic properties of Co surfaces.

II. COMPUTATIONAL METHODS

We have performed *ab initio* calculations within the local-density approximation, combining two different approaches. First, we have performed an exhaustive search of the equilibrium adsorption positions of H using slab models, a plane-wave basis set and the projector-augmented wave method[25] as implemented in the Vienna *ab initio* simulation package (VASP).[26] For the most stable configurations, we have then determined the electronic and magnetic properties within the fully-relativistic framework of the screened Korringa-Kohn-Rostoker (SKKR) method,[27] which allows for a smooth matching of the surface region to the semi-infinite bulk and lacks of the quantum size effects inherent to slab models.

For the calculations with VASP, an energy cutoff of 350 eV has been used. The structures are modeled by periodically repeated slabs of 6 to 10 Ru layers covered by two Co MLs on one side and adding 1/4 ML or 1 ML of H on top of or underneath the outermost Co layer. A vacuum region of 12 Å is left between both slab surfaces which prevents any spurious interaction between them. This model also guarantees the recovery of the bulk properties at the inner Ru layers of the slab. The search for the most stable H adsorption sites has been performed starting from different H geometries and allowing full relaxation of the atomic positions of H, Co, and the outermost Ru layer. A uniform sampling of the *k* mesh centered in Γ has been used, and convergence for the most stable structures has been obtained using *k* samplings of up to $(15 \times 15 \times 1)$ for (1×1) geometries and $(8 \times 8 \times 1)$ for the (2×2) unit cells corresponding to adsorption of 0.25 ML of H. Under these conditions, convergence in total-energy differences below 1 meV is achieved.

By using the optimized geometry with the most stable H adsorption sites, the detailed electronic structure and the magnetic moments were calculated in terms of the fully relativistic SKKR method.[27] The SKKR formalism provides, in a natural way, layer-resolved physical quantities such as charges and magnetic moments. It, thus, manifests a perfect tool for the analysis of the H-Co interactions and of the influence of the Co film thickness in the H-induced properties. For this purpose, we have extended our calculations to films of 3–6 Co MLs. Details of the SKKR calculations for the Co/Ru system can be found elsewhere.[24,28,29] The H atom is

TABLE I. Energy (in meV) per H atom with respect to the most stable fcc hollow site for different H adsorption sites on 2 ML Co on Ru(0001), both for 1 and 0.25 ML H coverage. The dependence on the in-plane lattice parameter a_{2D} and the stacking sequence of the Co film are shown for the high H coverage.

	Co film		H adsorbate		
	a_{2D} (Å)	Stacking	hcp	Bridge	Subsurface
1 ML	2.7	AB	27	289	>420
		BC	24	708	>430
	2.6	AB	27	278	>480
		BC	108	708	>550
0.25 ML	2.6	AB	45	236	>1000

modeled by using an atomic sphere of radius 0.59 Å, placed at the equilibrium distance to Co determined by VASP.

III. STRUCTURAL PROPERTIES

The stable adsorption site of H on 2Co/Ru(0001) has been explored starting from different geometries, depicted in Fig. 1: top, bridge, hollow, (either fcc or hcp) and off-symmetry positions, both at surface and subsurface sites. In addition, for 1 ML coverage, the influence of structural modifications present in the Co film has been considered, such as the variation in the 2D lattice parameter, or the existence of stacking faults which alter the Co/Ru stacking sequence from the hcp AB/AB to BC/AB.[30]

A summary of the results is compiled in Table I. In all cases, the most stable adsorption site corresponds to H at fcc hollow surface positions. The table shows the energy difference with respect to the equilibrium configuration only for the most stable structures. The rest of geometries considered, including on-top positions, provide total energies larger by more than 1 eV. Our results are in good agreement with previous ones relative to different Co surfaces and thin films:[16,18] H tends to stick at the surface trying to preserve the threefold symmetry of the Co lattice, independent of the detailed Co film structure or the H coverage. The energy difference between adsorption sites provides an estimate of the diffusion barriers for H in the surface. Although the trends are similar for all surfaces studied, partial H coverage or alteration of the stacking sequence at the Co film may modify the diffusion barriers significantly. Regarding subsurface sites, the barrier for the diffusion of H into the Co film decreases as the H coverage increases but it is always large enough to support the low probability of the penetration of H into the film, in good agreement with the experiments of thermal desorption through formation of H_2.[15]

The results indicate that the adsorption of H is governed by the local surface formation of strong H-Co bonds. Supporting this, for all structures considered the H-Co distance remains around 1.7 Å, independent of the H coverage and the Co film structure. The largest variations in the H-Co distance are found to depend on the H adsorption site, where H

TABLE II. Adsorption energy and work function for 2Co/Ru(0001), either bare or covered by H, together with the variation in the Co-Co and Co-Ru interlayer spacings relative to the unrelaxed Ru bulk, Δd_{CC} and Δd_{CR}, respectively. The two values of Δd_{CC} for 0.25 ML coverage correspond to Co atoms unbonded/bonded to H.

H coverage	E_{ads} (eV)	Φ (eV)	Δd_{CC} (Å)	Δd_{CR} (Å)
Bare		6.03	−0.29	−0.06
0.25 ML	3.34	6.09	−0.30/−0.27	−0.07
1 ML	3.41	7.02	−0.22	−0.09

is coordinated to a different number of Co atoms: from 1.5 Å for the on-top surface adsorption (coordination 1), to 1.9 Å for hollow subsurface sites (coordination 6).

A further insight can be obtained comparing the energetics and structure of the equilibrium configurations of the Co film covered by different amounts of H. From now on we will restrict our considerations to the experimental value of a_{2D}, 2.6 Å. The adsorption energy per H atom is defined as

$$E_{ads} = -\frac{1}{N_H}[E_{HCoRu} - E_{CoRu} - N_H E_H], \quad (1)$$

where N_H refers to the number of adsorbed H atoms per unit cell, E_{HCoRu} and E_{CoRu}, respectively, to the total energies of the slabs with and without adsorbed H and E_H to the energy of isolated H. The adsorption energies for the different H coverages are reported in Table II. Their positive sign indicates that adsorption is favorable in all cases. When comparing with the formation energy of the H_2 molecule, 2.44 eV/H atom, we can see that both H coverages are highly stable against desorption, in good agreement with the experimental evidence and the previous theoretical calculations for similar Co surfaces.[16,18] An alternative approach to determine the stability of the H covered surfaces comes from the evaluation of the work function, Φ, also provided in Table II as obtained with the SKKR method. The increase in Φ with H coverage, specially for the complete H overlayer, corroborates the large sticking coefficient of H at Co surfaces even for ultrathin films and is in good agreement with the results obtained for Co films on Cu(001).[18]

Table II also provides the variation in the interlayer spacings in the Co film. As expected from the reduced atomic volume of Co compared to Ru, even for the bare surface there is a significant contraction of the Co-Co interlayer distance, d_{CC}, trying to compensate the in-plane expansion. Accordingly, the Co-Ru distance, d_{CR}, is only slightly reduced. The large volume compensation effect suppresses the oscillatory relaxation of interlayer distances typical of transition-metal surfaces, although an oscillatory behavior can be identified in the layer-resolved electronic properties for larger Co thicknesses. Upon H adsorption, the progressive filling of free bonds attenuates the surface-induced relaxations but still the volume compensation remains. Thus, the resulting relaxation pattern is different from that of other H covered films where Co retains its 2D lattice constant.[18] In spite of this

difference, we can conclude that H always acts as an attenuator of surface effects. It is worth noticing the slight corrugation of 0.03 Å at the Co surface layer for 1/4 ML H coverage, driven by the Co atoms bonded and unbonded to H. Remarkably, the surface-induced contraction of d_{CC} is enhanced for those unbonded.

IV. ELECTRONIC AND MAGNETIC PROPERTIES

Next we discuss the layer-resolved electronic and magnetic properties of the 2 Co/Ru(0001) film with and without H coverage. The atom projected DOS and magnetic moments are shown in Fig. 2 and in Table III, respectively. The DOS of the bare film shows the narrowing induced by the reduced coordination at the surface plane. In the case of Co with the majority spin band almost full, this causes an increase in the magnetic moment. As H adsorbs, the surface effects start to attenuate, and, upon completion of 1 ML of H, the magnetization of the two Co layers becomes almost uniform. The H-states localize at the bottom of the d VB, and show a significant spin polarization induced by the hybridization with Co, even though the net magnetic moment of H is almost zero. In turn, H-induced features can be identified in a region dominated by sp states for the surface Co atoms bonded to H. The weight of these features for the rest of Co atoms, including those at the surface layer for 0.25 ML of H (not shown in the figure), is negligible.

The short range of the H-induced effects can also be inferred from the magnetic moments of the surface Co atoms bonded and not bonded to H for 0.25 ML coverage, see Table III. Noticeably, the partial H coverage results in a significant increase in the magnetic moments of the Co atoms unbonded to H. This is evidenced both in the fully relativistic calculations performed with the SKKR method and in those performed with slab models. Though the arbitrary assignment of the atomic radii affects the actual values of the magnetic moments for each atom, the relative differences between the structures calculated under the same conditions provide a reliable physical picture. Furthermore, the total magnetic moment per slab, which is not subject to the assignment of the individual atomic radii, also supports the enhancement of the surface magnetism for partial H coverages: $9.64\mu_B$ (bare), $10.88\mu_B$ (0.25 ML), and $9.72\mu_B$ (1 ML). This enhancement can be understood in terms of the strong local H-Co interaction, which limits the Co-Co interactions within the surface plane. Quite interestingly, similar trends for the orbital moments of the Co atoms upon H dosing can be inferred from Table III. From this we expect that the adsorption of H affects the magnetic anisotropy energy of the Co/Ru(0001) system in a nontrivial manner, as well.

Finally, we discuss the H-induced effects for thicker Co films. To this end, we performed SKKR calculations for Co films of up to 6 MLs covered by 1 ML of H. Figures 3 and 4 show, respectively, the layer-resolved values of the spin (m_S) and orbital (m_L) contributions to the magnetic moment for the different Co thicknesses, together with those at the corresponding bare surfaces. Upon H adsorption there is always a strong reduction in both m_S and m_L at the surface Co atoms. On average, the reduction is around $0.25\mu_B$ for m_S and
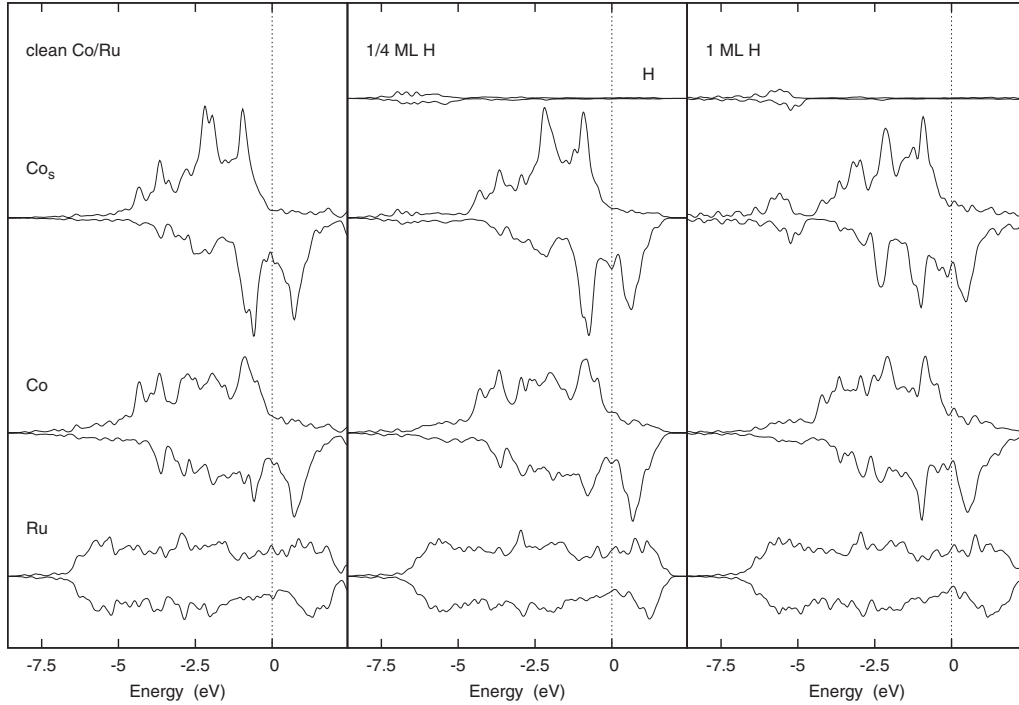
FIG. 2. DOS projected on the H, surface Co (Co$_s$), interface Co and Ru atoms of the 2Co/Ru(0001) surface system either bare (left) or covered by 1/4 ML (middle) and 1 ML (right) of H. The Co$_s$ DOS for 1/4 ML H coverage corresponds to Co atoms bonded to H. Energies are related to the Fermi level.

$0.04\mu_B$ for m_L. By contrast, at the subsurface Co layer the reduction in the magnetic moment is low, becoming negligible for the layers underneath. Although the specific values of m_S and m_L at each layer involve in a complex way the oscillatory layerwise variation in the electronic properties, the effect of H does not depend on the Co thickness. Furthermore, it is very similar for both components of the magnetic moment.

Not shown in the figure, in all cases the H atom acquires a m_S of $0.01\mu_B$, and no orbital polarization. Similarly, the components of the moment induced at the interface Ru atom are around $-0.02\mu_B(m_S)$ and $-0.001\mu_B(m_L)$ for all Co thick-

nesses, without any significant variation as compared to the bare film. The layer-resolved DOS (not shown here) are consistent with this conclusion, with H-induced features almost restricted to the surface Co layer in each case. Thus we can conclude that the H-induced effects are essentially restricted to the surface and independent of the Co thickness.

V. CONCLUSIONS

In terms of *ab initio* calculations, we performed a detailed theoretical analysis of the stability, electronic structure, and magnetism of Co/Ru(0001) films upon H adsorption. Our

TABLE III. Layer-resolved magnetic moments obtained with slab models (m_{slab}), as well as spin (m_S) and orbital (m_L) contributions to the magnetic moments calculated by the relativistic SKKR method for the 2Co/Ru(0001) surface system covered by different amounts of H. The moments are given in μ_B and the labels of the atoms are the same as in Fig. 2. For 0.25 ML H coverage, the moments of the Co atoms unbonded/bonded to H are distinguished.

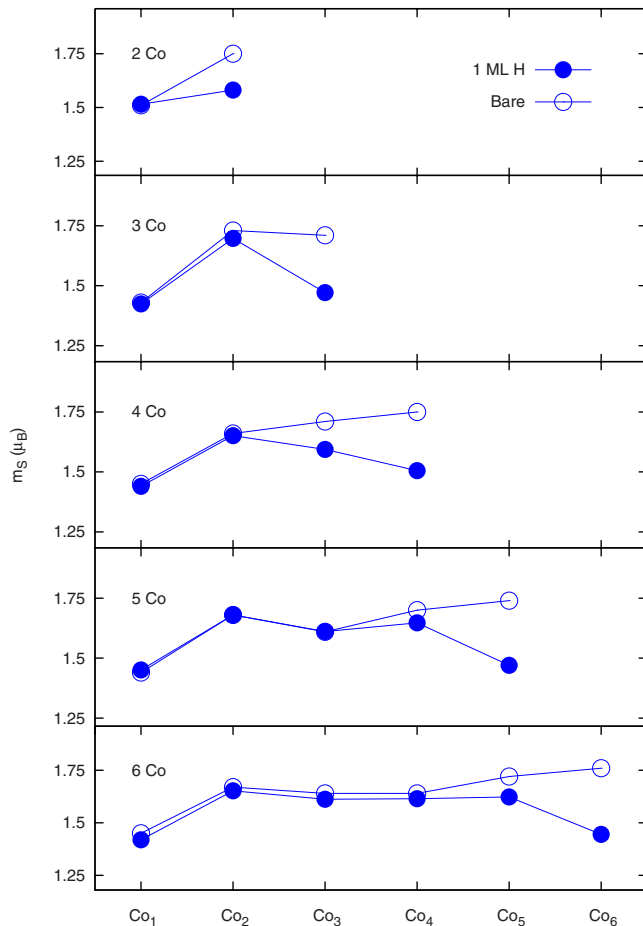|	Ru	Co	Co$_S$	H	
m_{slab}	−0.05	1.31	1.69		Bare
	−0.07	1.30/1.23	1.76/1.54	−0.02	0.25 ML
	−0.02	1.27	1.27	−0.01	1 ML
m_S	−0.03	1.51	1.75		Bare
	−0.01	1.56/1.50	1.94/1.75	0.04	0.25 ML
	−0.01	1.52	1.58	0.01	1 ML
m_L	0.00	0.08	0.11		Bare
	0.00	0.08	0.13/0.10	0.00	0.25 ML
	0.00	0.08	0.07	0.00	1 ML

FIG. 3. (Color online) Layer-resolved Co spin magnetic moment for Co films of 2–6 MLs (from top to bottom), either bare (empty circles) or covered by H (solid circles). Layers are numbered from the Ru interface.

FIG. 4. (Color online) Same as Fig. 3 for the orbital contributions to the magnetic moment.

main observations are as follows: H adsorbs on Co at the hollow sites by preserving the threefold symmetry of the system. The adsorption is endothermic for all H coverages with the largest binding energy corresponding to the complete H overlayer. Furthermore, the probability of H desorption or segregation is low. Concerning the structural, electronic, and magnetic properties, the effect of H has a local surface character and is almost independent of the detailed Co thickness and structure. H always attenuates surface effects. However, for partial H coverages, this leads to the enhancement of the surface-induced features for Co atoms
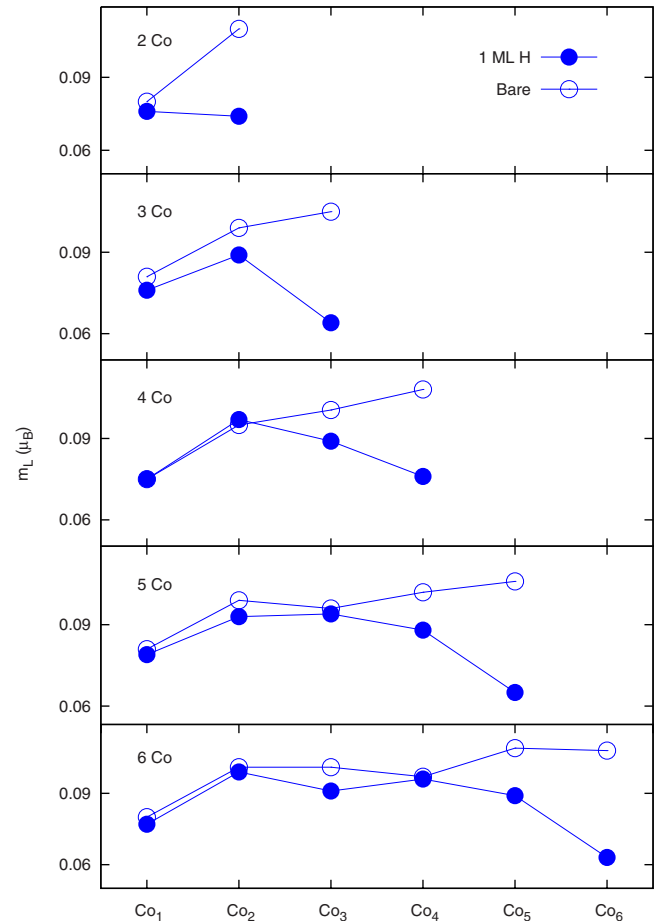
not bonded to H, and, in particular, to an enhancement of the net surface magnetic moment. Our results point to the importance of residual H in magnetic measurements and to the possibility for the reversible manipulation of the properties of ultrathin Co films and surfaces by tuning H adsorption.

[1] K. Christmann, Surf. Sci. Rep. **9**, 1 (1988).

[2] M. A. Vannice, J. Catal. **37**, 449 (1975), and references therein.

[3] J. K. Norsko, Rep. Prog. Phys. **53**, 1253 (1990), and references therein.

[4] U. Gradmann, J. Magn. Magn. Mater. **6**, 173 (1977).

[5] G. J. Mankey, M. T. Kief, F. Huang, and R. F. Willis, J. Vac. Sci. Technol. A **11**, 2034 (1993).

[6] F. R. Vukajlović, Z. S. Popović, A. Baldereschi, and Ž. Šljivančanin, Phys. Rev. B **81**, 085425 (2010).

[7] N. O. Jones, M. R. Beltran, S. N. Khanna, T. Baruah, and M. R. Pederson, Phys. Rev. B **70**, 165406 (2004).

[8] R. Hammerling, J. Zabloudil, and S. Gallego, Philos. Mag. **83**, 3159 (2003).

[9] D. Sander, W. Pan, S. Ouazi, J. Kirschner, W. Meyer, M. Krause,

S. Müller, L. Hammer, and K. Heinz, Phys. Rev. Lett. **93**, 247203 (2004).

[10] D. Sander, Z. Tian, and J. Kirschner, J. Phys.: Condens. Matter **21**, 134015 (2009).

[11] B. Hjörvarsson, J. A. Dura, P. Isberg, T. Watanabe, T. J. Udovic, G. Andersson, and C. F. Majkrzak, Phys. Rev. Lett. **79**, 901 (1997).

[12] S. Ostanin, V. M. Uzdin, C. Demangeat, J. M. Wills, M. Alouani, and H. Dreysse, Phys. Rev. B **61**, 4870 (2000).

[13] E. Kravtsov, A. Nefedov, G. Nowak, K. Zhernenkov, H. Zabel, B. Hjörvarsson, A. Liebig, A. Hoser, G. J. McIntyre, L. Paolasini, and A. Remhof, J. Phys.: Condens. Matter **21**, 336004 (2009).

[14] K. M. E. Habermehl-Cwirzen, K. Kauraala, and J. Lahtinen, Phys. Scr., T **108**, 28 (2004).

[15] M. Sicot, O. Kurnosikov, H. J. M. Swagten, and B. Koopmans, Surf. Sci. **602**, 3667 (2008).

[16] D. J. Klinke and L. J. Broadbelt, Surf. Sci. **429**, 169 (1999).

[17] K.-H. Ernst, E. Schwarz, and K. Christmann, J. Chem. Phys. **101**, 5388 (1994).

[18] A. A. Mubarak, B. A. Hamad, and J. M. Khalifeh, J. Magn. Magn. Mater. **322**, 780 (2010).

[19] A. L. Cabrera, W. Garrido-Molina, J. Colino, D. Lederman, and I. K. Schuller, Phys. Rev. B **55**, 13999 (1997), and references therein.

[20] F. Greuter, I. Strathy, E. W. Plummer, and W. Eberhardt, Phys. Rev. B **33**, 736 (1986).

[21] F. J. Himpsel and D. E. Eastman, Phys. Rev. B **20**, 3217 (1979).

[22] M. Sicot, O. Kurnosikov, O. A. O. Adam, H. J. M. Swagten, and B. Koopmans, Phys. Rev. B **77**, 035417 (2008).

[23] S. Pick and H. Dreysse, Surf. Sci. **460**, 153 (2000).

[24] F. El Gabaly, S. Gallego, C. Muñoz, L. Szunyogh, P. Weinberger, C. Klein, A. K. Schmid, K. F. McCarty, and J. de la Figuera, Phys. Rev. Lett. **96**, 147202 (2006).

[25] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[26] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993); **49**, 14251 (1994); G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11169 (1996).

[27] J. Zabloudil, R. Hammerling, L. Szunyogh, and P. Weinberger, *Electron Scattering in Solid Matter: A Theoretical and Computational Treatise* (Springer-Verlag, Berlin, 2005).

[28] F. El Gabaly, K. F. McCarty, A. K. Schmid, J. de la Figuera, M. C. Muñoz, L. Szunyogh, P. Weinberger, and S. Gallego, New J. Phys. **10**, 073024 (2008).

[29] S. Gallego, M. C. Muñoz, L. Szunyogh, and P. Weinberger, Philos. Mag. **88**, 2655 (2008).

[30] F. El Gabaly, J. M. Puerta, C. Klein, A. Saa, A. K. Schmid, K. F. McCarty, J. I. Cerda, and J. de la Figuera, New J. Phys. **9**, 80 (2007).