Experimental Evidence of Magnetic Ordering at the Rh(100) Surface

A. Goldoni,[1] A. Baraldi,[1] G. Comelli,[1,2] S. Lizzit,[1] and G. Paolucci[1]
[1]*Sincrotrone Trieste, s.s. 14 Km 163.5 in Area Science Park, 34012 Trieste, Italy*
[2]*Dipartimento di Fisica, Universita' di Trieste, Via Valerio 2, 34127 Trieste, Italy*
and Laboratorio Tecnologie Avanzate Superfici e Catalisi dell' Istituto Nazionale per la Fisica della Materia, Padriciano 99, 34012 Trieste, Italy
(Received 21 September 1998)

Clear evidence of magnetic ordering at the Rh(100) surface has been obtained by measuring the linear magnetic dichroism in the angular distribution of the Rh-3*d* photoelectrons. The experiment is performed by reversing the orientation of the magnetic moments using an external magnetic field and observing the difference in the core level line shape. Since the Rh-3*d* levels exhibit a clearly resolved surface component, it is possible to associate the changes to magnetic ordering restricted to the surface layer. [S0031-9007(99)08954-1]

PACS numbers: 75.30.Pd, 79.60.Bm

It is well known that 4*d* and 5*d* transition metal elements do not exhibit ferromagnetic order in the bulk. However, several theoretical studies [1–12] have suggested that magnetism in reduced dimensionality (films, surfaces, or small clusters) is not *a priori* restricted to those elements exhibiting magnetism in the bulk. A good candidate to investigate low dimension magnetic effects is the paramagnetic 4*d* element Rh. In fact, bulk Rh is already very close to satisfying the Stoner criterion of ferromagnetism [1,13], and, because of the lower number of nearest-neighbor atoms, the *d*-derived band width in low dimensional Rh systems is considerably narrower than in the bulk. The increased density of states at the surface or in small clusters, therefore, is likely to stabilize the magnetic state in these low dimensional structures. Indeed, experimental results [14] confirm that clusters of Rh formed by 9–36 atoms exhibit a magnetic moment reaching a maximum value of $1.1\mu_B$. These clusters, which were at equilibrium and at temperatures around 100 K, are superparamagnetic: that is, their magnetic moment orients itself freely along the applied magnetic field and completely ignores the atomic (crystalline) arrangement of the building atoms. These experimental observations have found correspondence in many theoretical approaches [7,12]. Theory also predicts that one monolayer of Rh would be magnetic if it could be grown pseudomorphic on either Au(100), Ag(100), or C(0001) surfaces [1–6,8–12], but experimental testing of this prediction did succeed only partially [15–18].

The situation is much more controversial in the case of the Rh(100) surface. Surface magnetism has been invoked [19] to explain the small relaxation of the Rh(100) first intralayer spacing obtained experimentally by three independent low-energy electron diffraction (LEED) studies [20]. The experimental value for the first-layer relaxation is between -1.6% and $+1.5\%$, while theoretical calculations without the inclusion of magnetic effects [19,21,22] give a relaxation between -5.1% and -3.8%. The *ab initio* calculation by Morrison *et al.* [19] finds that the first two layers of the Rh(100) surface are ferromagnetic with a magnetic moment of $1.8\mu_B$, resulting in a "magnetic pressure" that reduces the intralayer relaxation to -1.52%, in good agreement with LEED results. This theoretical prediction of surface magnetism in Rh(100) has been questioned by calculations of Weinert *et al.* [23] which demonstrate, for the case of the Fe(001) surface, the inaccuracy of the pseudopotentials used in Ref. [19]. In addition, recent first principle calculations [12], while confirming the magnetic properties of Rh clusters isolated or deposited on Ag(100), predict the absence of magnetism at the Rh(100) surface, in agreement with other theoretical work [22]. It is worth noting, however, that all of these calculations are done within the local-density approximation (LDA), which does not describe properly the magnetic state. To overcome this LDA limitation, Cho and Scheffler [13] have performed a new theoretical study based on the generalized gradient approximation. This approach gives a relaxation of -1.4% if the vibrational contribution to the free energy for $T \neq 0$ (not included in previous works) is taken into account. The latter result is, therefore, in very good agreement with LEED measurements [20] even without the inclusion of surface magnetism. Nevertheless, Cho and Scheffler show that the ferromagnetic state is practically degenerate with the nonmagnetic state if the magnetic moment is lower than $0.6\mu_B$ (while the ground state is nonmagnetic for the magnetic moment $\geq 0.6\mu_B$) suggesting that a weak ferromagnetic state, possibly stabilized by defects, can occur at the Rh(100) surface. Spin resolved valence band photoemission measurements [24] seem to suggest that the Rh(100) surface may be weakly ferromagnetic at room temperature. However, as pointed out by others [12,13], this experimental evidence is far from being conclusive. In particular, our experience indicates that the cleaning procedure adopted in Ref. [24] does not ensure a clean and well-ordered surface. In conclusion, the presence of magnetic phenomena in Rh thin films or at the (001) surface is still awaiting a clear experimental proof.

 0031-9007/99/82(15)/3156(4)$15.00

In this Letter we report on linear magnetic dichroism in the angular distribution (LMDAD) in core level photoemission experiments on Rh(100) by means of linearly polarized synchrotron light. At a given experimental geometry, the photoemission spectra were acquired for two opposite orientations (up and down) of the magnetic field applied parallel to the sample surface. In the presence of sample magnetization, this provides a series of mirror experiments for testing LMDAD [25,26]. We found that in chiral geometry (i.e., the magnetic field perpendicular to the photoemission scattering plane) the surface component in both the Rh-3d core levels shows evident dichroism, providing a clear experimental evidence of magnetism in the Rh(100) topmost layer.

The experiments were carried out in an ultrahigh vacuum (UHV) chamber (base pressure 5×10^{-11} mbar) at the SuperESCA beam line using linearly polarized photons delivered by the 5.6 undulator of the ELETTRA storage ring in Trieste. A clean and well-ordered (100) surface of a Rh single crystal, previously annealed at high temperature in a hydrogen furnace and then repolished, was prepared by cycles of Ar^+ sputtering and annealing up to 1300 K in UHV, followed by oxidation and reduction in 10^{-7} mbar of oxygen and hydrogen, respectively. These treatments were repeated until a sharp LEED pattern was observed and no contaminants were detected by x-ray photoemission. The sample closed the gap of a horseshoe yoke electromagnet. The magnetic field was applied parallel to the sample surface both perpendicular to the photoemission scattering plane (chiral geometry) and parallel to the scattering plane (nonchiral geometry), by means of a current ramp through the electromagnet coil. The measurements have been performed when the current was off, with a residual magnetic field of about 13 G on the sample, which does not extend away from the sample surface. The photoelectrons were collected by a 150 mm hemispherical analyzer, with $\pm 2°$ of angular acceptance. The angle between the impinging photons and the analyzer was fixed at 40°. All the photoemission spectra were acquired by keeping the sample at 100 K with an overall energy resolution better than 60 meV.

In order to measure surface properties, we must identify surface related features in the photoemission spectra. As it is well known, the $3d_{5/2}$ core level of the Rh(100) surface presents a quite clear surface core level shifted component [27]. Figure 1 shows the Rh-$3d_{5/2}$ core level spectra, for two different experimental geometries, taken with a photon energy of 396 eV and null magnetization. These spectra are in excellent agreement with the best Rh-$3d_{5/2}$ spectra already published [27]. The peak at a lower binding energy is enhanced in the more surface sensitive conditions and, therefore, is the surface component. The surface peak is strongly quenched by any small amount of contaminants present on the surface (even when they are below the photoemission detection limit). We found that even in the very clean vacuum of our chamber the surface peak was partially quenched after a few minutes. For this reason, the cleaning procedure has been repeated after the acquisition of two spectra only (i.e., after one cycle of the magnetic field). The very high flux and fast acquisition rate of the SuperEsca beam line allow the recording of these core level spectra in less than 3 min. This fact, together with an efficient sample cooling (less than 5 min to reach 100 K after the cleaning procedure), guarantees the cleanliness of the surface during data acquisition.

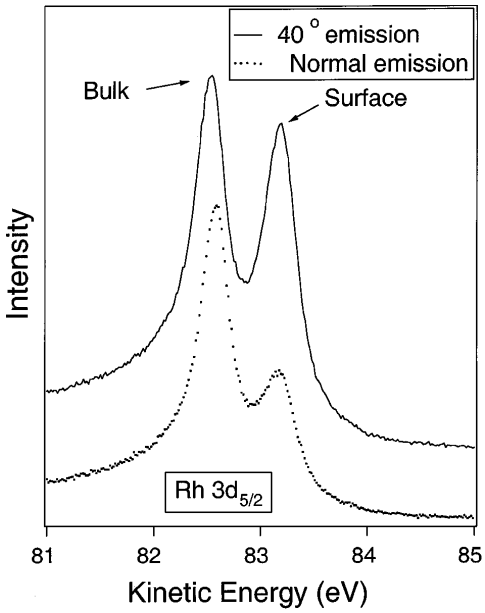

FIG. 1. Rh-$3d_{5/2}$ core level photoemission spectra obtained for two different experimental geometries. Surface and bulk core components are indicated. The origin of the binding energy scale is set to the Rh(100) Fermi edge.

By applying the magnetic field and reversing it by 180°, it is possible to create two mirror experiments that allow LMDAD effects in core level photoemission spectra in the presence of sample magnetization and chirality [25,26]. The dichroism in the core level is determined by the existence of spin polarization in the core photohole induced by spin-orbit coupling and by the multiplet splitting of the photoemission final state due to the exchange and Coulomb interactions of the photohole with the spin-polarized valence electrons [25,26]. LMDAD can be identified by measuring the spectroscopic asymmetry A created in core level photoemission by flipping the magnetization from M_{up} to M_{down}. The asymmetry A is defined as $A = (I_{\mathrm{up}} - I_{\mathrm{down}})/(I_{\mathrm{up}} + I_{\mathrm{down}})$, where I_{up} and I_{down} are the spectral intensities measured when the magnetic field is up or down, respectively. Obviously, the absence of magnetic effects implies $I_{\mathrm{up}} = I_{\mathrm{down}}$ and, therefore, vanishing A.

Figure 2(a) shows the whole Rh-3d spectra taken at $h\nu = 396$ eV for the two mirror geometries M_{up} (solid line) and M_{down} (points) in normal emission. The two spectra have been normalized to the same background

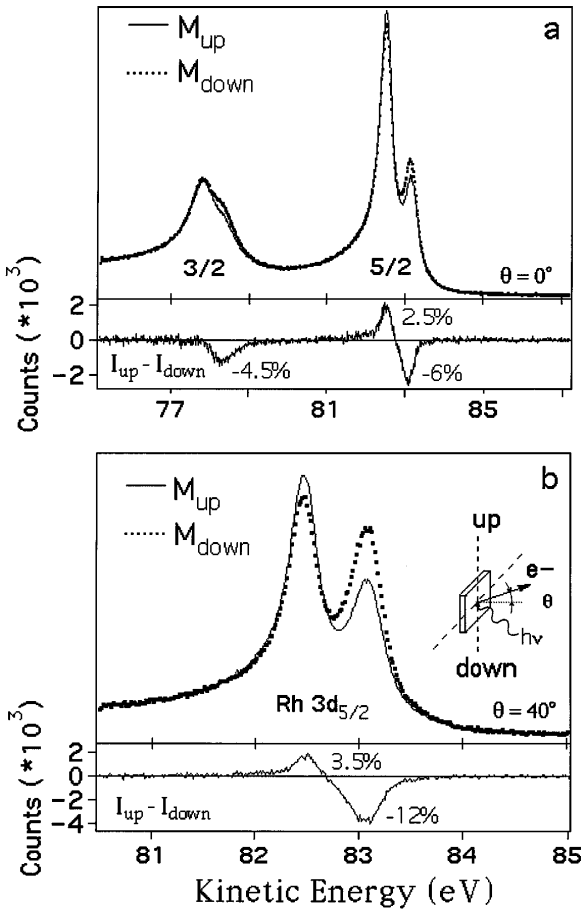

FIG. 2. (a) Rh-3d core level photoemission spectra obtained at normal emission upon reversing the magnetization from M_{up} to M_{down} in chiral geometry. (b) Rh-3$d_{5/2}$ core level photoemission spectra obtained at 40° of emission upon reversing the magnetization. The difference $I_{\mathrm{up}} - I_{\mathrm{down}}$ is plotted in the bottom panels. The resulting peak asymmetries A, as defined in the text, are also reported.

intensity in the spectral regions above the Rh-3$d_{3/2}$ and below the Rh-3$d_{5/2}$ core levels. Figure 2(b) shows the Rh-3$d_{5/2}$ core level region, taken in more surface sensitive conditions. These spectra show clear LMDAD effects as evidenced by the difference $(I_{\mathrm{up}} - I_{\mathrm{down}})$ plotted at the bottom. The maximum asymmetry is in correspondence of the surface peak. The evidence of a surface Rh-3d core level asymmetry indicates the presence of an axial asymmetry induced by surface magnetization. Even though bulk Rh is paramagnetic, we observe an asymmetry also in the region of the bulk component of the Rh-3$d_{5/2}$ photoemission spectrum, suggesting that the complex multiplet structure of the surface 3$d_{5/2}$ peak spans over the whole core level spectrum. This is not surprising since the 3d core hole state of angular momentum $J = \frac{5}{2}$ is split by the Coulomb and exchange interaction with the 4d valence electrons into sublevels with a given projection m_J along the surface magnetization quantum axis. Splittings ranging from a few tens of meV up to 1 eV have been calculated for transition metals [26]. Moreover, from Fig. 1 it is clear that there is a surface contribution also in the bulk peak region, being the bulk peak larger and shifted to lower kinetic energy in the more surface sensitive spectrum.

In Fig. 2(a) we note that the 3$d_{3/2}$ and 3$d_{5/2}$ core levels do not exhibit opposite LMDAD. Actually, a change of the sign is not necessarily expected for the emission from d levels ($l = 2$). In this case, in fact, the LMDAD asymmetry is proportional to the superposition of two fundamental spectra, namely, I^1 and I^3 (see Ref. [26]), whose relative weight is angular dependent. A similar behavior was predicted, for example, on the 3d levels of Tm [26]. Moreover, it has been discussed in Ref. [28] that dichroism in crystalline solids cannot be described in terms of atomic effects only, as magnetic elastic scattering (photoelectron diffraction) plays a crucial role in such systems.

However, since the measurements have been performed in the presence of a residual field, particular care was taken to exclude artifacts possibly related to the presence of the field. First of all, we have verified that by applying the magnetic field in the photoemission scattering plane (i.e., in a nonchiral geometry), there are not effects induced on the photoemission spectra by reversing the magnetic field. Figure 3(a) shows the 3$d_{3/2}$ and 3$d_{5/2}$ core levels taken at normal emission, upon reversing the magnetic field in nonchiral experiments. For these spectra the asymmetry is zero, confirming the absence of LMDAD in nonchiral geometry.

To further rule out any instrumental artifact, we verified the absence of LMDAD in a sharp core level of a nonmagnetic system. The latter was obtained by deposition on the Rh(100) surface of a saturated layer of CO molecules. It is known that adsorption of CO on both Ni surface and Ru monolayers strongly reduces or completely quenches the atomic magnetic moments [29], and a similar effect has been predicted in the case of adsorption on Rh monolayers on graphite substrate [29]. Furthermore, even on ferromagnetic surfaces the magnetic interaction between CO molecules and the substrate is very weak and no LMDAD of the C-1s core level is expected [30]. Figure 3(b) shows the C-1s photoemission spectra of the CO saturation coverage on Rh(100) taken upon reversing the magnetic field in chiral experiments. To avoid possible effects due to the analyzer transmission, the photon energy has been chosen so that the C-1s electron kinetic energy is the same as for the Rh-3d photoelectrons of Fig. 2. Noteworthy, the line shape of the two C-1s photoemission spectra of Fig. 3(b) is the same and no LMDAD effects are observed, as shown by the null asymmetry plotted under the spectra. In addition, the C-1s core level of the saturation coverage of CO/Rh(100) shows sizable photoelectron diffraction effects, which are comparable to those of the Rd-3$d_{5/2}$ core level of the clean surface. The results shown in Fig. 3,

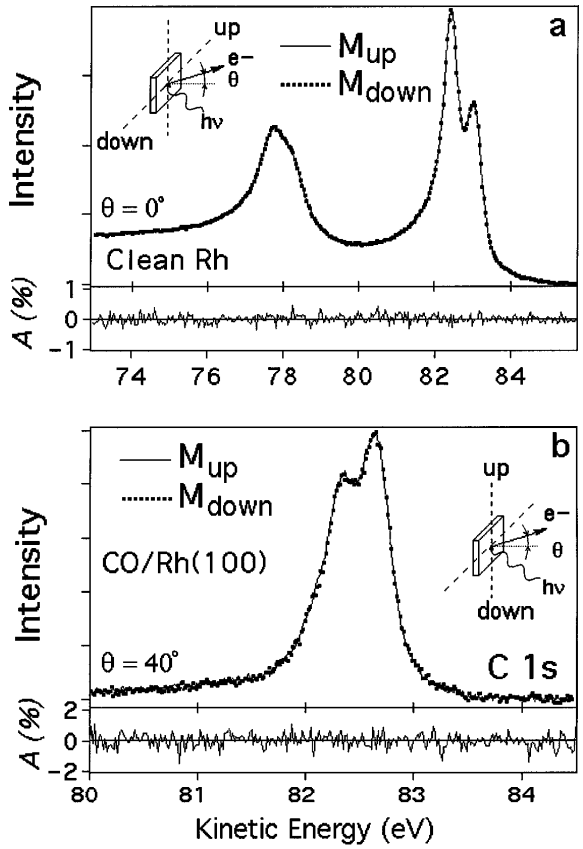

FIG. 3. (a) Rh-3*d* core level photoemission spectra obtained upon reversing the magnetization from M_{up} to M_{down} in nonchiral geometry, taken at normal emission. (b) C-1*s* core level photoemission spectra of a saturation coverage of CO on Rh(100) obtained upon reversing the magnetization in chiral geometry. The bottom panels show the corresponding asymmetries.

therefore, clearly indicate that the observed LMDAD on the 3*d* core levels of clean Rh(100) is a genuine effect.

In conclusion we have shown that evident LMDAD is present in the surface component of the 3*d* core level photoemission spectra of Rh(100) upon reversing the magnetic field in chiral experiments. This constitutes the first clear experimental evidence of magnetic ordering at the Rh(100) surface.

We thank G. Rossi and M. Altarelli for helpful discussions.

[1] V. L. Moruzzi and P. M. Marcus, Phys. Rev. B **39**, 471 (1989).
[2] O. Eriksson, R. C. Albers, and A. M. Boring, Phys. Rev. Lett. **66**, 1350 (1991).
[3] M. J. Zhu, D. M. Bylander, and L. Kleinman, Phys. Rev. B **43**, 4007 (1991); L. Kleinman, Int. J. Mod. Phys. **7**, 482 (1993).
[4] S. Blügel, Phys. Rev. Lett. **68**, 851 (1992); Europhys. Lett. **18**, 257 (1992).
[5] R. Q. Wu and J. A. Freeman, Phys. Rev. B **45**, 7222 (1992); **51**, 15 131 (1995).
[6] A. Mokrani *et al.*, J. Magn. Magn. Mater. **113**, 201 (1992).
[7] B. V. Reddy, S. N. Khanna, and B. I. Dunlap, Phys. Rev. Lett. **70**, 3323 (1993); Yang Jinlong *et al.*, Phys. Status Solidi B **195**, 553 (1996); B. Piveteau *et al.*, Surf. Sci. **352**, 951 (1996).
[8] J. Redinger, S. Blügel, and R. Podloucky, Phys. Rev. B **51**, 13 852 (1995).
[9] B. Ujfalussy, L. Szunyogh, and P. Weinberger, Phys. Rev. B **51**, 12 836 (1995).
[10] P. Krüger *et al.*, Physica (Amsterdam) **237B & 238B**, 278 (1997).
[11] L. Chen *et al.*, J. Appl. Phys. **81**, 4161 (1997).
[12] S. K. Nayak *et al.*, Phys. Rev. B **56**, 8849 (1997).
[13] J.-H. Cho and M. Scheffler, Phys. Rev. Lett. **78**, 1299 (1997).
[14] A. J. Cox, J. G. Louderback, and L. Bloomfield, Phys. Rev. Lett. **71**, 923 (1993); A. J. Cox *et al.*, Phys. Rev. B **49**, 12 295 (1994).
[15] H. Li *et al.*, Phys. Rev. B **44**, 1438 (1991).
[16] G. A. Mulhollan, R. L. Fink, and J. L. Erskine, Phys. Rev. B **44**, 2393 (1991).
[17] C. Liu and S. D. Bader, Phys. Rev. B **44**, 12 062 (1991).
[18] H. Beckmann and G. Bergmann, Phys. Rev. B **55**, 14 350 (1997).
[19] I. Morrison, D. M. Bylander, and L. Kleinmen, Phys. Rev. Lett. **71**, 1083 (1993).
[20] P. R. Watson *et al.*, Surf. Sci. **72**, 562 (1978); W. Oed *et al.*, Surf. Sci. **207**, 55 (1988); A. Begley *et al.*, Phys. Rev. B **48**, 12 326 (1993).
[21] M. Methfessel, D. Hennig, and M. Scheffler, Phys. Rev. B **46**, 4816 (1992).
[22] J.-H. Cho and M.-H. Kang, Phys. Rev. B **52**, 13 805 (1995); A. Eichler *et al.*, Surf. Sci. **346**, 300 (1996).
[23] M. Weinert, S. Blügel, and P. D. Johnson, Phys. Rev. Lett. **71**, 4097 (1993).
[24] S. C. Wu *et al.*, Phys. Rev. B **49**, 14 081 (1994).
[25] Ch. Roth *et al.*, Phys. Rev. Lett. **70**, 3479 (1993); G. Rossi *et al.*, Solid State Commun. **90**, 557 (1994); G. Rossi, F. Sirotti, and G. Panaccione, in *Core Level Spectroscopies for Magnetic Phenomena*, NATO ASI, Ser. B, Vol. 345 (Plenum, New York, 1995), p. 181; F. U. Hillebrecht *et al.*, J. Magn. Magn. Mater. **148**, 49 (1995).
[26] B. T. Thole and G. van der Laan, Phys. Rev. B **49**, 9613 (1994); G. van der Laan, in *Core Level Spectroscopies for Magnetic Phenomena* (Ref. [25]), p. 153.
[27] M. Zacchigna *et al.*, Surf. Sci. **347**, 53 (1996).
[28] A. Fanelsa *et al.*, Solid State Commun. **96**, 291 (1995); R. Schellenberg *et al.*, Phys. Rev. B **57**, 14 310 (1998).
[29] C. S. Feigerle *et al.*, Phys. Rev. Lett. **56**, 2207 (1986); P. W. Selwood, *Chemisorption and Magnetism* (Academic Press, New York, 1975); P. Pfandzetter, G. Steierl, and C. Rau, Phys. Rev. Lett. **74**, 3467 (1995); K. C. Hass, M.-H. Tsai, and R. V. Kasowski, Phys. Rev. B **53**, 44 (1996).
[30] M. Getzlaff, J. Bansmann, and G. Schönhense, J. Chem. Phys. **103**, 6691 (1995).