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Electronic structure and magnetism of the Rh{001} surface

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Spin-polarized-photoemission experiments on clean Rh{001} show that the surface resonance at the $\bar{M}$ point (0.60 eV binding energy) in the surface Brillouin zone is weakly ferromagnetic at room temperature. The effect increases with decreasing temperature of the surface and disappears when the surface is covered with 0.5 layer of oxygen. The spin- and angle-resolved photoemission spectra exhibit very small exchange splitting, hence the magnetic moment of the surface atoms cannot be reliably determined, but is estimated to lie between $0.1\mu_B$ and $0.2\mu_B$.

It is well known that $4d$ and $5d$ transition metals do not exhibit ferromagnetic ordering in the bulk. Among the $4d$ elements, however, rhodium is particularly interesting because, although it is paramagnetic in the bulk, it exhibits ferromagnetic properties when prepared in low-dimensional forms. Theory predicts it to be ferromagnetic if it could be grown as a pseudomorphic monolayer on either Au{001} or Ag{001}.[1,2] Experiments aimed at testing this prediction did not succeed for different reasons. On Au{001}, pure and uniform overlayers of Rh could indeed be grown epitaxially, but not pseudomorphically. On Ag{001}, continuous films could not be grown because the Rh islands, although pseudomorphic with the substrate, were either covered by or intermixed with Ag atoms. But in the very early stages of growth a 4.1 ± 0.3-eV splitting of the $4s$ levels were detected, which was not observed in thick Rh films.[3] This splitting was explained by the presence of a magnetic moment in the Rh atoms and related to the theoretical prediction mentioned above. Other experimental studies of Rh films grown on Fe{001} confirmed the theoretical predictions that a monolayer of Rh grown on this ferromagnetic substrate would have a magnetic moment of the order of $0.82\mu_B$, i.e., similar to that predicted for the monolayer on a silver substrate.[4] Another unrelated but equally interesting experimental result is that in clusters of Rh with 12–32 atoms, magnetic moments ranging between $0.3\mu_B$ and $1.1\mu_B$ were detected at 93 K.[5]

A recent *ab initio* pseudopotential calculation of a nine-layer Rh slab, by Morrison, Bylander and Kleinman[6] (MBK) finds that the surface and the first subsurface layer are ferromagnetic with a magnetic moment of $1.8\mu_B$. The resulting "magnetic pressure" reduces the relaxation of the first interlayer spacing on Rh{001} from -3.22% in the paramagnetic case to -1.52% (Ref. 6). The same relaxation was calculated by Feibelman and Hamann[7] to be -5.1% without consideration of magnetic effects. The relaxation value of MBK is in much better agreement with the results of three independent low-energy electron diffraction (LEED) analyses[8] of Rh{001} which fix the first-layer relaxation between -1.2% and $+0.5\%$. However, MBK's finding of ferromagnetism in the top two layers of Rh{001} is disputed by calculations of Weinert, Blügel, and Johnson (WBJ), who show that the use of the valence pseudocharge only, as done by MBK, leads to unrealistically large magnetic moments and susceptibility values in Fe{001}. Thus, WBJ believe that ferromagnetism of the Rh{001} surface is unlikely.[9]

The work reported herein was motivated by the desire to test MBK's prediction experimentally by means of spin-polarized photoemission. The work involved two stages: the first was concerned with the identification of surface-sensitive parameters that would allow the study of surface properties independently of the bulk, i.e., the identification of surface states and surface resonances on Rh{001}; the second was concerned with the measurement of the magnetic properties of the surface by spin-polarized photoemission. The results indicate that the surface of Rh{001} is only weakly ferromagnetic. The observed spin polarization would suggest that the magnetic moment in the first layer is between $0.1\mu_B$ and $0.2\mu_B$.

The spin-polarized experiments reported here were carried out in an apparatus described in detail elsewhere.[10] We mention here only that the exciting radiation was provided by the vacuum-ultraviolet undulator of Beamline U5 at the National Synchrotron Light Source, and spin measurements were made with a compact low-energy spin detector also described elsewhere.[11] The angular resolution of the hemispherical analyzer was $\pm1.5°$ and the combined photon and analyzer energy resolution was 0.35 eV.

The Rh{001} surface was cleaned *in situ* with repeated

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cycles of argon-ion bombardments and anneals (at about 600 °C). Surface cleanness was monitored by means of photoelectron spectroscopy with special attention to contamination by CO and O. The crystallinity of the surface was checked with LEED. After the cleaning procedure the Rh{001} surface remained clean only for a relatively short period—a contamination peak due to CO became visible in the photoemission spectra approximately 20 min after the annealing step. The surface was then cleaned again by flashing the sample to about 200 °C for 5 min. This operation was repeated every 20 min to keep the surface free of adsorbed CO.

In order to be able to measure surface properties—in the present case, surface magnetism—we must first identify the location of filled surface states or surface resonances, if any, in the surface Brillouin zone. That surface states are to be found on Rh{001} is expected from the calculations of Gay, Smith, and Arlinghaus,[12] who used the self-consistent local-orbital method to conclude that a large percentage of the electrons in the surface region of Rh{001} are in surface states. In support of the theoretical predictions, Morra, Almeida, and Willis[13] reported the observation of a strong surface state immediately below the Fermi level at the $\bar{M}$ point of the surface Brillouin zone of Rh{001}.

In the present work we look for surface states both along the $\bar{\Gamma}$-$\bar{M}$ line and the $\bar{\Gamma}$-$\bar{X}$ line, although we report here only the results pertinent to the $\bar{\Gamma}$-$\bar{M}$ line (the results for the $\bar{\Gamma}$-$\bar{X}$ line are equivalent). Figure 1 shows angle-resolved electron-distribution curves near the $\bar{M}$ point for an incident energy of 71 eV. The spectrum from the clean surface exhibits a large peak just below the Fermi level E_F at an approximate binding energy of 0.6 eV. Experiments done with different incident angles of the synchrotron radiation demonstrate that this peak is sensitive to s-polarized light. Exposure of the surface to oxygen up to a coverage of approximately 0.5 shows that the clean surface peak stems from two contributions: one from a bulk direct transition from the initial Σ_3 band and one from a surface resonance near the $\bar{M}$ point. Again, the existence of this occupied surface resonance is consistent with the theoretical calculations.

Having established surface sensitivity in the photoemission at the $\bar{M}$ point, we proceed to examine the possible magnetism of the corresponding electron states by monitoring the appropriate spin-polarized angle-resolved electron-distribution curves.

In Fig. 2 we show the spin-resolved spectra recorded at the $\bar{M}$ point at room temperature before and after exposure to oxygen. The clean-surface spectra in Fig. 2, upper panel, show a spin polarization of the order of 4% in the peak immediately below the Fermi level. Although not shown here, the spin polarization increases on cooling the sample to about 200 K. Exposure of the surface to 0.5 L (1 L=10^{-6} Torr sec) of oxygen reduces the spin polarization to zero as shown in Fig. 2, lower panel. This latter observation suggests that the source of polarization is surface derived.

One possible source of spin polarization would be the presence of magnetic impurities on the surface of the Rh sample. However, no detectable impurity level was found

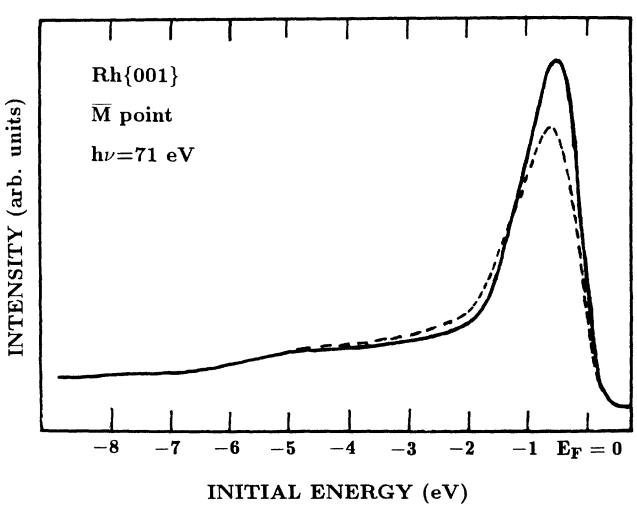

FIG. 1. Angle-resolved electron-distribution curves near the $\bar{M}$ point of the surface Brillouin zone of Rh{001} measured with photon energy $h\nu$ = 71 eV, 35° incidence (67% s-polarized light) and 23° emission angle. Solid curve, clean surface; dashed curve, surface covered with 0.5 layer of oxygen.

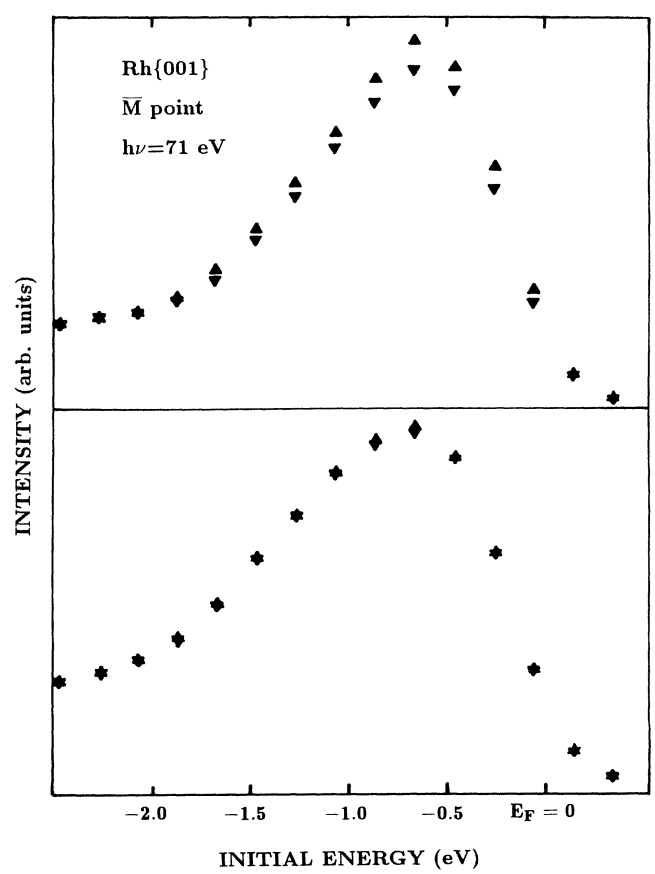

FIG. 2. Spin- and angle-resolved electron-distribution curves at the $\bar{M}$ point measured with photon energy $h\nu$ = 71 eV. Majority and minority components are indicated with triangles pointing up and down, respectively. Above, clean surface; below, surface contaminated with about 0.5 layer of oxygen.

using core-level photoemission. Another possibility is that the polarization derives from a spin-orbit-induced splitting in the vicinity of the Fermi level. Indeed, such polarization effects have been observed in several photoemission studies from nonmagnetic materials using both polarized and nonpolarized incident radiation.[14] However, the fact that we apply a magnetizing pulse to the sample in opposite directions and observe a reversed polarization suggests that the spin-orbit effects are not the source of polarization in the present case.

In Fig. 2 the exchange splitting—the difference in peak positions of spin-up and spin-down curves—is almost undetectable, estimated to be at most 0.1 eV. This very small exchange splitting indicates that the magnetic moment of Rh atoms in the first layer of the sample surface is very small. A quantitative estimate of its magnitude is difficult to make with confidence, but we nevertheless attempt a rough estimate in two ways, one by means of a comparison with known ferromagnetic materials and one by using the measured polarization values.

In Fe and Co the magnetic moments are $2.2\mu_B$ and $1.7\mu_B$, respectively, while the corresponding exchange splittings of the Δ_5-symmetry $3d$ band are 2.2 eV for bcc Fe (Ref. 14) and 1.2 eV for fcc Co (from inverse photoemission[15]). If we assume a simple Stoner-like approximation, we may relate the exchange splitting Δ to the magnetic moment m such that $\Delta = Um$, where U is the effective Stoner parameter for the particular element. This procedure provides a reasonable description of the Fe and Co exchange splittings. If we consider Rh with a Stoner parameter calculated to be 0.65 eV,[16] an exchange splitting of 0.1 eV translates into a moment of the order of $0.15\mu_B$.

Another estimate of the magnitude of the magnetic moment can be attempted from the value of the spin polarization P which we may define as

$$P \propto \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow},$$

where $N_\uparrow$ and $N_\downarrow$ represent the numbers of spin-up and spin-down electrons in the system. The total number of d electrons in metallic Rh is 8. If the measured polarization is 2–4 % then the above equation yields a moment of 0.15–$0.30\mu_B$. However, this approximation is only really valid for the measured background polarization and furthermore it reflects the value adopted for the Sherman function of the spin detector.

In conclusion, the experiments described herein indicate that a clean Rh{001} surface may be weakly ferromagnetic at room temperature. This result was obtained by measuring the spin polarization of a surface resonance at the $\bar{M}$ point. It is difficult to provide any reliable quantitative estimate of the surface moments from valence-band photoemission. However, any approximation suggests that the magnitude is much smaller than that calculated by MBK. Hence, the large discrepancy between the surface relaxation of Rh{001} calculated by Feibelman and Hamann without including magnetic effects (−5.1%, Ref. 7) and that measured by LEED (−1.2% to +0.5%, Ref. 8) cannot be explained by the weak ferromagnetism of the Rh{001} surface found herein, and therefore remains unsettled. We note, however, that recent calculations of the relaxation of the first interlayer spacing on Rh{001} find smaller values than found by Feibelman and Hamann: Methfessel, Henning, and Scheffler[17] find −3.5% and Kraft[18] finds −2.2%.

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