Two-Dimensional Ferromagnetism of 3*d*, 4*d*, and 5*d* Transition Metal Monolayers on Noble Metal (001) Substrates

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Ferromagnetism of 5*d* transition metal monolayers is predicted for the first time. For Ir on Ag and Au (001) magnetic moments of $0.9\mu_B$ were found by *ab initio* calculations based on the full-potential linearized augmented-plane-wave method. Os is magnetic on Ag but nonmagnetic on Au. Comparing 5*d* magnetism with 4*d* and 3*d* results, a remarkable trend emerges: The element with the largest moment among the 3*d*, 4*d*, and 5*d* monolayers is shifted from Mn to Ru (isoelectronic to Fe) and to Ir (isoelectronic to Co), respectively. 4*d* and 5*d* magnetism is explained as a true two-dimensional band-structure effect.

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Itinerant magnetism in three dimensions (3D) is observed for metals and compounds synthesized with elements of the 3*d* transition metal series; in particular, Cr, Mn, Fe, Co, and Ni. Magnetism is also obtained for solids with elements of the 4*f* and 5*f* series. But their electrons responsible for the magnetically ordered phases do not participate in the Fermi surface and they present examples of localized spin systems. In general, magnetism for Sc, Ti, V, 4*d*, and 5*d* metals is not observed. Exceptions are materials such as the weakly ferromagnetic compounds $ZrZn_2$ [1], Sc_3In [2], or, for instance, some of the invar alloys (e.g., Fe_3Pt) where small magnetic moments are induced on 4*d* or 5*d* sites by 3*d* elements.

In fact, Gunnarsson [3] and Janak [4] investigated the possibility of spontaneous magnetizations for 4*d* metals. They found that with intra-atomic exchange integrals I_{4d} of about 0.65 eV and local densities of states (LDOS) n_{loc} at the Fermi energy (E_F) varying from 0.32 state/spin eV for Mo to 1.15 states/spin eV for Pd, the Stoner criterion $n_{\text{loc}}(E_F)I > 1$ is never satisfied for any 4*d* metal. Following the general trend of decreasing localization of valence *d* wave functions when moving from the 3*d* to 4*d* and 5*d* series we find, consequently, an increase of the *d*-band width and a reduction of LDOS $n_{3d} > n_{4d} > n_{5d}$ at the Fermi energy. Together with the fact that the exchange integral also decreases as $I_{3d} > I_{4d} > I_{5d}$, 5*d* magnetism becomes extremely unlikely and was never considered.

Itinerant magnetism in two dimensions (2D) is not *a priori* restricted to those elements which exhibit magnetism in 3D. Because of the reduced coordination number of nearest-neighbor atoms the *d*-band width in 2D is considerably smaller than in 3D [5-8] and the magnetic instability should occur for a much wider variety of transition metal elements. Superimposed are 2D band-structure effects. These effects are caused by the interference of Bloch wave functions and depend on their phase and on the crystal structure. They are expected to play an important role in stabilizing a magnetic phase. In 3D they are responsible for the magnetism of fcc Ni or the large susceptibility of Pd [9], but for the paramagnetism of artificial bcc Ni. Transition metal monolayers grown on noble metal substrates form approximate experimental realizations of 2D itinerant magnets. The noble metal *d* band is well below the Fermi energy and the influence on magnetism due to the monolayer-substrate *d*-*d* interaction is small. A large variety (e.g., Co/Au, Fe/Ag, Fe/Au, Mn/Ag, Cr/Ag, and V/Ag [10]) of 3*d* metals at the one monolayer range have been stabilized experimentally. But, surprisingly, no 4*d* or 5*d* system has been investigated. Particularly for 5*d* monolayer magnetism—if it exists—one would expect new results on the magnetocrystalline anisotropies and thermodynamical properties due to the combination of magnetism and large spin-orbit interaction.

Very recently several groups reported theoretical predictions of 4*d* monolayer ferromagnetism for Tc [11], Ru [11,12], and Rh [11-13] on Ag and Au (001) substrates, with large magnetic moments of about $1.7\mu_B$ [11] and $1.0\mu_B$ [11,13] for Ru and Rh, respectively. Mo and Pd [11,12,14] monolayers remained nonmagnetic on these substrates. This Letter is concerned with a systematic search for ferromagnetic 5*d* transition metal monolayers on noble metal substrates. For the arguments given below it is sufficient to concentrate only on Re, Os, and Ir as possible 5*d* candidates. As noble metals we have chosen Ag and Au (001) substrates. The lattice mismatch between monolayer and substrate is smaller than 7% and it should be possible to grow these systems. Cu is excluded as a possible substrate, since the lattice mismatch is too large. The arguments for 5*d* monolayer magnetism on Ag and Au apply also to a Cu_3Au substrate, which has an even smaller lattice mismatch of about 2%, but it is not considered here. In this Letter evidence of itinerant 5*d* transition metal magnetism in two dimensions is presented for the first time. We find that Ir on Ag(001) and Au(001) is ferromagnetic with surprisingly large magnetic moments of $0.91\mu_B$ and $0.94\mu_B$, respectively. Os is magnetic on Ag(001) ($0.34\mu_B$) but nonmagnetic on Au(001). When comparing these results with previous calculations for 3*d* [8,15] and 4*d* metal [11] monolayers on Ag(001) and Au(001) a remarkable trend is observed: The element with the largest magnetic moment among each transition metal series is shifted from Mn to Ru (isoelectronic to Fe) and at last to Ir (isoelectronic to Co) among the 3*d*, 4*d*, and 5*d* series, respectively. Following these trends we do not expect ferromagnetism for any other 5*d* metal on noble metal (001) substrates and, indeed, Re remained nonmagnetic. These trends also reveal the differences in monolayer magnetization when choosing Ag or Au as a possible substrate.

The results are obtained with the full-potential linearized augmented-plane-wave (FLAPW) method [16] for film geometry. Seven-layer (001) films consisting of five layers Ag or Au and one 5*d* metal monolayer on each surface are considered. Among the cutoff parameters inherent in the FLAPW method, the magnetic moment depends most strongly on the accuracy of the Brillouin-zone integration. The magnetic moments and total-energy differences between ferromagnetic and paramagnetic solutions are monitored by performing calculations with an increasing number of $k_\parallel$ points until final convergence is obtained for 78 special $k_\parallel$ [17] in the irreducible wedge of the 2D Brillouin zone. Core states are calculated fully relativistically and valence states are treated scalar. The calculations apply density-functional theory using the local spin-density approximation of von Barth and Hedin [18], in the parametrization of Moruzzi, Janak, and Williams [19]. The monolayer-substrate interlayer spacing is taken to be the average of their bulk lattice spacings $a_0^{5d\text{-sub}} = \frac{1}{2}(a_0^{5d}/2 + a_0^{\text{sub}}/2)$.

Figure 1 shows the spin-split LDOS obtained for Fe and Co [8], and for their isoelectronic 4*d* [11] and 5*d* elements Ru, Rh and Os, Ir on Ag(001), respectively, all resulting from ferromagnetic calculations. The major features in each panel arise from well-defined monolayer *d* bands of these transition metal atoms. Comparing monolayers in the sequence 3*d* to 4*d* to 5*d* elements one observes that the *d*-band width broadens in steps of about 1 eV from about 1.5 to 3.5 eV. This is a consequence of the significantly increasing overlap of the *d* orbitals within the monolayer when moving from 3*d* to 5*d* transition metals. However, in all cases the *d*-band width is substantially narrower than that of the corresponding metallic bulk values. This is consistent with the argument that an increasing coordination number of *d* metal atoms causes band broadening and prevents the 4*d* and 5*d* bulk metals from being magnetic. In accordance with the increasing *d*-band width the exchange splitting is reduced substantially. One observes, for instance, an exchange splitting of about 3, 1, and ≈0 eV for Fe, Ru, and Os monolayers, respectively. In this connection two points

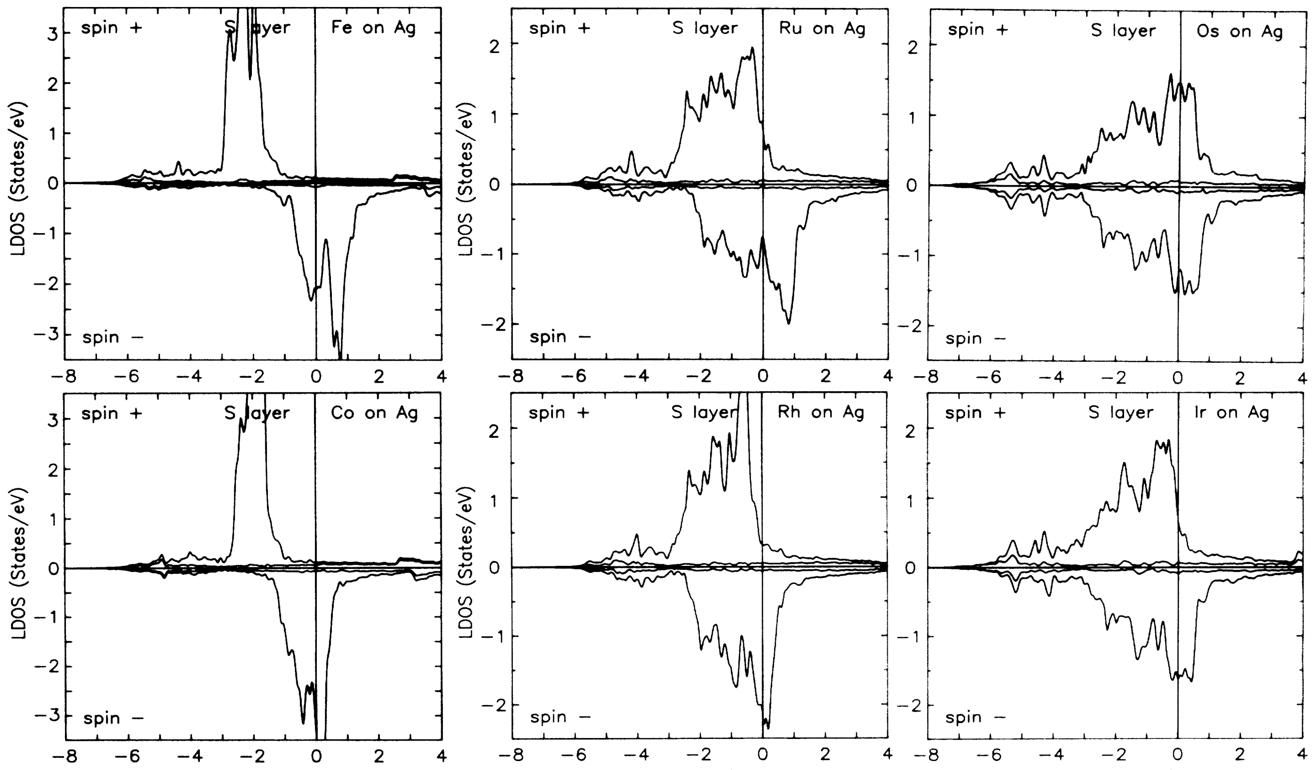

FIG. 1. Local densities of states (LDOS) together with the insignificant sum of $s+p+f$ contributions for ferromagnetic Fe, Ru, Os and Co, Rh, Ir monolayers on Ag(001). Shown are the LDOS for the majority (+) and minority (−) spin directions. Notice that for Fe and Co the scale of LDOS is chosen differently.

are noteworthy: First, because of the stronger localization of the *d* wave functions at the end of each transition metal series, the *d*-band width of the Co, Rh, and Ir monolayers is always smaller than the bands of their corresponding neighboring elements Fe, Ru, and Os. As a consequence Ir is, together with Fe, Co, Ru, and Rh, a strong ferromagnet (majority band filled), but for Os the bandwidth is already too broad and it is a weak one with a small magnetic moment of $0.34\mu_B$. For Re, a neighbor of Os, the bandwidth already becomes too large for ferromagnetism. Tc on Ag is the analog of Os among the 4*d* metals, but shifted to the left in the periodic table. It is also a weak ferromagnet with a similar moment of $0.21\mu_B$. Second, the LDOS for antibonding states (typically located in the upper third of the *d* band) is much higher than for bonding states. This 2D band-structure effect stabilizes the 4*d* and 5*d* monolayer magnetism for late transition metals on noble metal substrates and explains together with the *d*-band broadening the absence of ferromagnetism of the early 4*d* and 5*d* metal monolayers. Further support for this view comes from results of Willenborg, Zeller, and Dederichs for 4*d* [20] and 5*d* [21] impurities and dimers in bulk Ag. They found that Mo and Tc impurities are magnetic, but nonmagnetic as dimers, and further that Ru and Rh are nonmagnetic as impurities and dimers, and at last that none of the 5*d* impurities are magnetic. These results are in line with our interpretation that monolayer magnetism of Mo and Tc disappears due to band broadening and the magnetism of Ru, Rh, Os, and Ir is stabilized due to interference effects in the 2D planar (001) lattice.

Collecting all the results on local moments for 5*d*, 4*d* [11], and 3*d* [8,15] monolayers on Ag(001) [see Fig. 2(a)], the general trend emerging is quite clear: Mn, Ru, and Ir show the largest moment among the 3*d*, 4*d*, and 5*d* metals, respectively. The magnetic moments of Ti, Tc, and Os are rather small and depend very likely on details such as, e.g., the experimental growth conditions. Pd and Pt are predicted to be nonmagnetic. Here the controlling parameter is the *d-sp* hybridization between the monolayer and substrate, which reduces already the moment of Ni as a monolayer on Ag. The overall picture of monolayers on Ag and Au is the same. But detailed calculations of 4*d* and 5*d* monolayers on Ag and Au (001) [Fig. 2(b)] show that due to the higher *d* band of Au with respect to Ag the monolayer-substrate *d-d* interaction increases, decreasing the LDOS of the monolayer bonding states and pushing the antibonding states slightly up. Therefore, Tc and Os are no longer magnetic on Au and at the same time the magnetic moment of Rh and Ir increases slightly from $1.02\mu_B$ and $0.91\mu_B$ on Ag to $1.10\mu_B$ and $0.94\mu_B$ on Au, respectively. As examples, the LDOS of Os on Ag and Au (001) resulting from paramagnetic calculations are shown in Fig. 3. There, the effect of the stronger hydridization between Os and Au as compared to Ag is clearly visible.

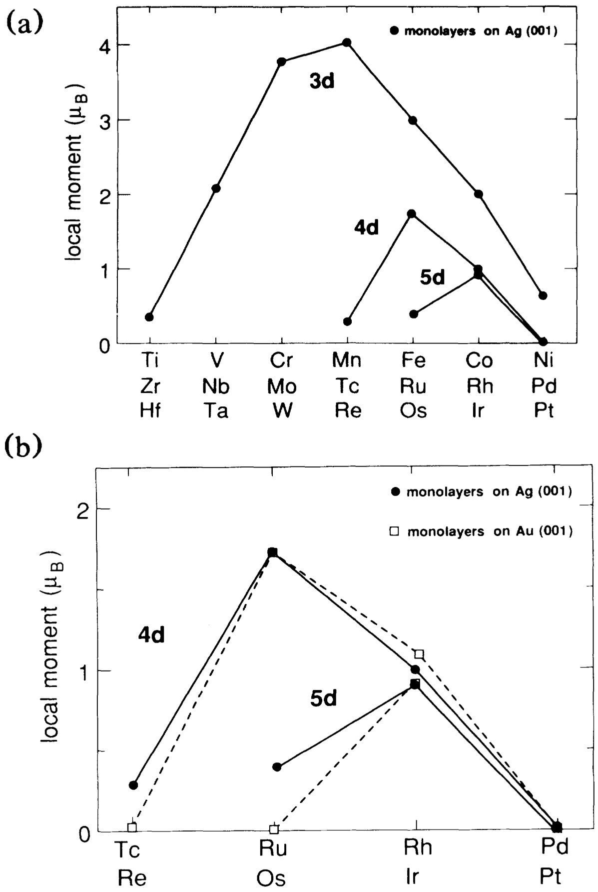

FIG. 2. Local magnetic moments as calculated for ferromagnetic (a) 3*d*, 4*d*, and 5*d* monolayers on Ag(001), and (b) 4*d* and 5*d* monolayers on Ag(001) (solid circles connected by solid lines) and Au(001) (open squares connected by dashed lines).

The ferromagnetic state of Ir/Ag, Ir/Au, and Os/Ag is their magnetic ground state. First their ferromagnetic total energies are lower than their paramagnetic ones by 1.0, 1.6, and 0.3 mRy per monolayer atom, respectively, and second the previously investigated $c(2\times2)$ antiferromagnetic configuration [22,23] should apply only for the early transition metals within each series (e.g., V, Cr, Mn among the 3*d* series). However, with the probable exceptions of Mo, Tc, and Re, the bands of the early 4*d* and 5*d* metals are already too broad for antiferromagnetism. Because of the combination of large spin-orbit interaction and big local moments, the large overlap of the 4*d* and 5*d* orbitals, and the fact that the magnetism disappears in 3D, interesting effects are foreseen for the magnetocrystalline anisotropies, critical temperatures, and critical exponents of Ru, Rh, and, in particular, Ir monolayers. Spin-orbit-induced modifications of the moment are expected to be small [24] and are neglected here. Changing the substrate from Ag or Au to Pd has shown drastic reductions of the 4*d* monolayer moment [11]. Similar

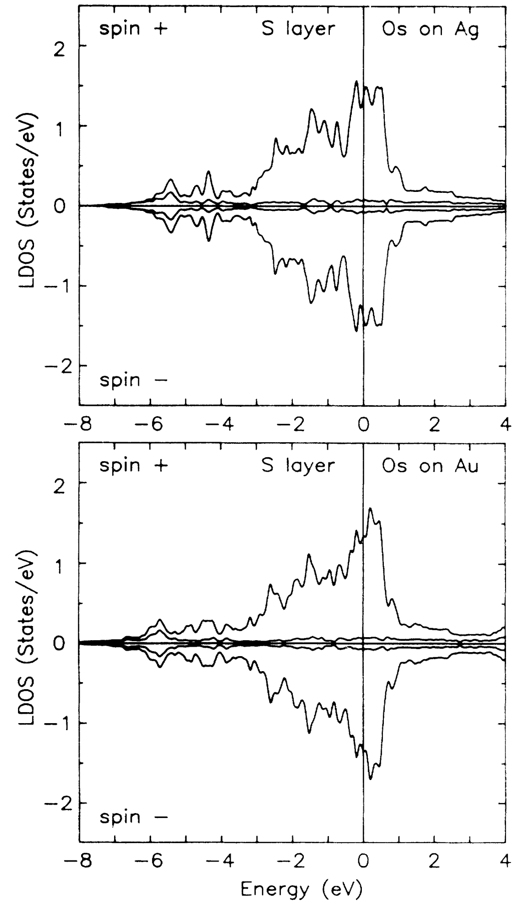

FIG. 3. Local densities of states (LDOS) together with the insignificant sum of $s+p+f$ contributions for Os on Ag(001) and Os on Au(001) obtained from a paramagnetic calculation.

changes will occur for 5*d* monolayers; controlling a layer by layer growth mode seems important to prove these predictions experimentally.

In summary, detailed calculations for Re, Os, and Ir on the (001) surfaces of Ag and Au have been performed. We found ferromagnetic solutions for Ir and Os on Ag, as well as Ir on Au. When comparing 3*d* with 4*d* and 5*d* monolayers we see that for consecutive transition metal series the in-plane *d*-*d* overlap increases and magnetism becomes less and less probable. However, 2D band-structure effects raise the LDOS for antibonding states, which stabilize 4*d* and 5*d* magnetism for some late transition metal monolayers. Moving along each transition metal series the number of holes decreases, and at the same time the bands are narrowing, because of the increasing localization of the wave function, making ferromagnetism progressively more likely but with smaller moments. At the end of the 4*d* and 5*d* series Pd and Pt monolayers are nonmagnetic again. The large hybridization between their *d* orbitals and the *sp* electrons of the noble metal substrates is the controlling parameter. The superposition of these trends explains the important observation that the most favorable condition for obtaining monolayer magnetism among the 3*d*, 4*d*, and 5*d* metals shifts from Mn to Ru (isoelectronic to Fe) and to Ir (isoelectronic to Co).

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