Prediction of Strongly Enhanced Two-Dimensional Ferromagnetic Moments on Metallic Overlayers, Interfaces, and Superlattices

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(Received 19 March 1985)

Strongly enhanced two-dimensional ferromagnetic moments are predicted for $3d$ bcc transition metals as overlayers and/or sandwiches and superlattices with Au and Ag. These range (in Bohr magnetons) from (i) 3.70 for Cr/Au(001), 2.96 for Fe/Ag(001), and 2.0 for V/Ag(001) for the overlayers, to (ii) 3.10 for the Au/Cr/Au sandwich and 2.95 for the Cr/Au superlattice, and to (iii) 3.1 for Cr on Fe/Au(001) and 2.30 for Fe on Cr/Ag(001). Surprisingly, a sizable moment ($0.14\mu_B$) is induced onto neighboring Au atoms. The noble metals play an optimal role as an almost ideal substrate which allows two-dimensional magnetism to occur.

PACS numbers: 75.30.−m, 73.40.−c, 73.60.Dt

Magnetism at surfaces and interfaces of transition metals continues to attract considerable experimental and theoretical attention. The reduced symmetry, the lower coordination number, and the availability and role of highly localized surface and interface states offers the possibility of inducing new and exotic phenomena and may hold out the promise of new device applications. A key question and goal has been the possibility of inducing two-dimensional (2D) magnetism in a controlled way. The availability of recently developed sophisticated synthesis and characterization techniques makes observation of such phenomena in laboratory-made structures such as overlayers, epitaxial sandwiches, and modulated structures (artificial superlattices) a challenging possibility. Concurrently, all-electron theoretical approaches have been developed—notably the total-energy full-potential linearized augmented plane-wave (FLAPW) method[1]—which give highly precise descriptions of the electronic, magnetic, and structural properties of thin films and bulk solids. The lively interplay of theory and experiment has already yielded interesting results. Thus, for example, enhanced magnetism at Fe,[2] Ni,[3] and Cr[4] surfaces has been predicted and observed. As regards interface magnetism in, say, bimetallic systems, however, it is generally believed and (so far) observed that in the absence of large negative-pressure effects, such as arise from lattice parameter mismatches,[5] a nonmagnetic metal would diminish the magnetism, if any, of the other metal.

We report here results of extensive FLAPW investigations which predict enhanced 2D magnetism in a number of transition-metal–noble-metal systems. Our findings include the unexpected theoretical prediction of (i) very large ferromagnetic moments ($3.70\mu_B$/atom) in monolayers of Cr on Au(001), (ii) the ferromagnetism of monolayers of V and Fe on Ag(001) and Fe on Cu(001), all with substantial moments ($2.0\mu_B$, $2.96\mu_B$, and $2.85\mu_B$, respectively), (iii) the relatively small reduction of the Cr magnetic moment (to $3.10\mu_B$/atom) when sandwiched between Au layers or when formed into a Cr-Au superlattice with Au of varying thickness, and (iv) a sizable magnetic moment [$(0.10–0.14)\mu_B$] induced onto neighboring Au atoms. These results are all the more remarkable when compared with the bulk versus surface (001) values for the clean transition metals: (0.59 versus 2.49)μ_B for Cr,[4] (2.15 versus 2.98)μ_B for Fe,[2] and (0 versus 0)μ_B for V.[6] Further, the consistency of the results indicates that true 2D magnetism is formed in these systems. These predictions, thus far on only a fraction of various combinations possible, are part of a growing literature which indicates the range and wealth of magnetic phenomena available for experimental investigation by a variety of techniques.

The all-electron local-spin-density-functional equations are solved self-consistently by means of the FLAPW method[1] (for single slab geometry) and the linear muffin-tin orbital method[7] (for the coherent modulated structure). In both approaches, the core electrons are treated fully realtivistically, and the valence states are calculated semirelativistically.[8] For the seven- (nine-) layer slabs, lattice harmonics with angular momentum components $l \leq 8$ are included to describe the charge and potential within the touching muffin-tin spheres: The wave functions are expanded in about 2×300 (350) LAPW basis functions. We employ[9] the explicit form of von Barth and Hedin for the local spin exchange-correlation potential and the Hedin-Lundqvist potential for the paramagnetic case.

Consider first the Cr_m-Au_n system for which a large number of configurations have been investigated for different numbers of atomic layers, m and n. When the plane of Au(001) is rotated by 45° with respect to that of Cr(001) there is an exact matching[10] of their primitive 2D square nets, because the experimental lattice constant of Cr (2.88 Å) is exactly a factor of $\sqrt{2}$ smaller than that of Au (4.08 Å); the stacking has atoms in the fourfold hollow site of adjacent atomic planes. Since the work of Brodsky *et al.*[10] has raised the possibiilty of the formation of fcc Cr when sandwiched by Au, we first carried out FLAPW total-

energy determinations of the Cr-Cr, Cr-Au, and Au-Au interlayer spacings. We found that (i) just one layer away from the Cr/Au interface, the Au fcc structure and the Cr bcc structure are retained; (ii) the Cr-Au interlayer spacing is close to the average of the bulk bcc Cr and fcc Au spacings—a result long suspected by materials scientists.

Selected results for the magnetic moments calculated within each atomic sphere at the Au/Cr interface are presented in Table I. As an aid in understanding the underlying physics and to emphasize its 2D nature, we focus first on results for the experimentally unattainable free monolayer Cr(001) film. A large magnetic moment of $4.12\mu_B$ is obtained which is close to the atomic limit and substantially larger than that of bulk antiferromagnetic Cr metal ($0.59\mu_B$). This is simply related to the band narrowing of the d band due to the reduced coordination number and lower symmetry for the monolayer. Surprisingly, when a monolayer of Cr(001) is deposited onto Au(001), the magnetic moment of the Cr overlayer decreases by only a small amount from the free monolayer value to $3.70\mu_B$. This extremely large moment—the largest value reported for a transition metal other than for Mn—is 50% greater than that of the surface layer in Cr(001) predicted theoretically[4] ($2.49\mu_B$) or derived experimentally[4] ($2.4\mu_B$). Also surprising is the finding that this substantially enhanced moment is only moderately reduced (to $3.10\mu_B$) when the Cr overlayer is itself covered by a Au layer. A very similar result was obtained, $2.95\mu_B$ per Cr atom, when the (1×1) Cr/Au coherent modulated structure was studied with the linear muffin-tin orbital approach (Table I). Since Cr is a notorious getter, the retention of this enhanced 2D magnetization in either the single sandwich or superlattice structures might make its observation much easier. Further, additional studies (not reported here) show that the Cr magnetic moment is hardly affected by the increase of Au thickness; more layers of Au tend to reduce the antiferromagnetic coupling between the ferromagnetic monolayer sheets in the superlattice geometry. Thus, there is the added degree of freedom

TABLE I. Theoretical layer by layer magnetic moments (in μ_B) for specified cases (with estimated uncertainties of $\pm0.03\mu_B$). S and $(S-n)$ indicate surface and subsurface layers. The last column shows the spin-polarization energy (in eV). CMS, coherent modulated structure.

	Cr	Nearest Au	E(para.) $-E$(spin-pol.)
Cr monolayer	4.12	...	1.69
1 Cr/Au(001) overlayer	3.70	0.14	0.78
2 Cr/Au(001)	2.90 (S), −2.30 ($S-1$)	−0.08	0.60
Au/Cr/Au(001) sandwich	3.10	0.14 (S), 0.13($S-2$)	0.38
(1×1) Au/Cr CMS	2.95	0.10	0.25
	Fe	Nearest Cu, Ag, Au	
Fe monolayer	3.20	...	1.34
1 Fe/Cu(001)	2.85	0.04	0.70
1 Fe/Ag(001)	2.96	0	1.14
2 Fe/Ag(001)	2.94 (S), 2.63 ($S-1$)	0.05	1.15
Ag/Fe/Ag	2.80	0	0.88
Au/Fe/Au	2.92	0.08	0.97
	V	Nearest Ag,Au	
1 V/Au(001)	1.75	0.04	0.10
1 V/Ag(001)	1.98	0.06	0.14
2 V/Ag(001)	1.15 (S), <0.05 ($S-1$)	0	0.08
Ag/V/Ag	0	0	...
Cr/Fe/Au(001)	3.10 (Cr), −1.96 (Fe)	−0.04 (Au)	0.68
Fe/Cr/Ag(001)	2.30 (Fe), −2.40 (Cr)	−0.09 (Ag)	0.52

of variable wavelength of modulation—and magnetic coupling—which may be important for technical applications including magnetic recording. Significantly, there is also a sizable magnetic moment induced onto neighboring Au atoms [$(0.10–0.14)\mu_B$] indicating a large magnetic perturbation of the Au induced by the magnetic Cr atoms. As in the case of the Cr atoms, the polarization of the Au atoms is mainly from the *d*-like electrons: The contribution from the *s*- and *p*-like electrons is only 1%–2% of the total. Only one layer away from the interface, the electronic structure of Au is essentially unperturbed and the structure and properties of bulk Au are retained.

To provide a better understanding of the mechanism behind the strongly enhanced magnetic moment formation on the Cr sites, we show in Fig. 1 the layer density of states (LDOS) within the muffin-tin sphere of Cr (in the paramagnetic state) for the Cr(001) monolayer [Fig. 1(a)], the Cr/Au(001) overlayer [Fig. 1(b)], and the Au/Cr/Au(001) sandwich [Fig. 1(c)]. It is seen that the basic feature of the sharp LDOS peaks about E_F remains similar as the number of Au atoms which are nearest neighbors to a Cr atom increases, except for some transfer of the LDOS to states lying at lower energy due to the enhanced hybridization between the Au and Cr *d* bands. It should be noted, however, that the center of the Au *d* band lies too far below E_F (about 4.5 eV) to have an effective interaction with Cr-localized surface (or interface) states in the vicinity of E_F. A calculation by Feibelman and Hamann[11] has also confirmed that the interface states of Cr/Au at E_F retain the same feature of the surface states for clean Cr(001). Moreover, the broadening effect of the LDOS peak due to the *s*-*d* hybridization is weakened by the very low LDOS of Au at E_F (~ 0.25 state/eV). For these reasons, the Cr overlayer on Au(001) or the Cr monolayer sandwiched by Au essentially retain much of the 2D electronic properties of a monolayer Cr(001) film. As a result of this electronic isolation, the high LDOS at E_F leads to a "Stoner" instability and drives the Cr layer to be ferromagnetic. The occupied portion of the Cr-localized energy bands are of predominantly majority-spin character. The derived exchange splittings are 3.8, 3.0, 2.5, and 2.4 eV for the Cr(001) monolayer, Cr/Au(001) overlayer, Au/Cr/Au(001) sandwich, and Cr/Au superlattice respectively.

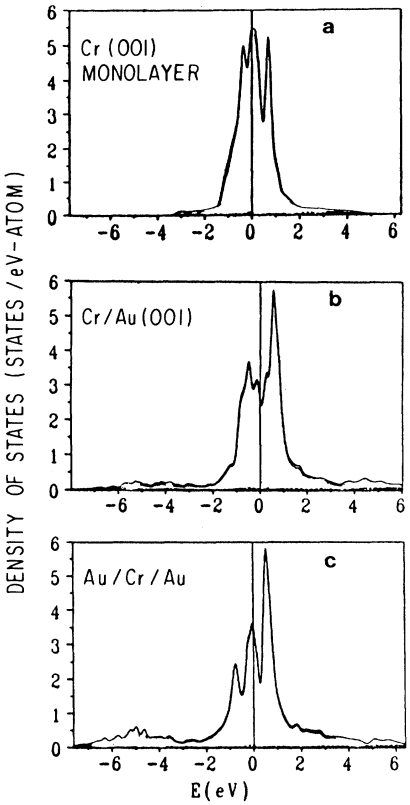

FIG. 1. Layer-projected partial density of states in units of states/eV-atom in the paramagnetic state of Cr(001) monolayer, Cr monolayer on Au(001) [Cr/Au(001)], and sandwich [Au/Cr/Au(001)].

The magnetic passivity of the Au and the independence of the Cr magnetic moment with increasing nonmagnetic Au layer thickness is in remarkable contrast with the effects of adding additional magnetic Cr layers: The magnetic moment of these single-Cr-layer structures is substantially decreased with increasing number of Cr layers. For example: (i) With two layers of Cr deposited on Au(001), the magnetic moment of the surface and subsurface Cr atoms are $2.9\mu_B$ and $-2.3\mu_B$, respectively; (ii) with three layers of Cr *sandwiched* on each side by two Au layers, the magnetic moments of the interface and subinterface Cr atoms are reduced to $1.75\mu_B$ and $-1.07\mu_B$; (iii) with five layers of Cr *sandwiched* on each side by two Au layers, moments are further reduced to $1.55\mu_B$, $-0.77\mu_B$, and $0.67\mu_B$ for interface, subinterface, and center Cr atoms, respectively. (Note that the moment in the center layer is now quite close to that of bulk Cr.)

Similar investigations have also been performed for monolayers of Fe and V adsorbed on Ag(001). For Fe-Ag there is a close matching of the lattice constants but a 5% mismatch for V-Ag or -Au. As in the case of Cr/Au(001), large magnetic moments, $2.96\mu_B$ (Fe) and $2.0\mu_B$ (V), are found for the adsorbate monolayers. The magnetic moment of the Fe overlayer on Ag(001) is remarkably close to the theoretical magnetic moment of the surface layer of an Fe(001) film ($2.98\mu_B$)—again indicating a lack of interaction with the substrate. The result for V/Ag(001) is much more surprising since, like the bulk, the surface layer of V(001) is not magnetic.[6] We thus have the remarkable prediction that an overlayer of V on Ag(001) is mag-

netically ordered with a sizable magnetic moment ($1.98\mu_B$) which is almost as large as the moment of Fe in bulk Fe. (If confirmed, this will be the first solid material for which elemental vanadium demonstrates magnetic ordering.) The origin of magnetic ordering is not negative pressure since, in fact, the matching to the Ag(001) substrate results from a *reduced* lattice constant for V by 5%. For both the Fe and V overlayers, we find—despite some hybridization between the *d* bands of the adsorbate and substrate—that the adsorbate-localized surface state bands retain their quasi-2D behavior for these systems. This behavior is further demonstrated for a monolayer of Fe sandwiched by Ag(001). The magnetic moment of Fe is only slightly decreased from that of the overlayer of Fe/Ag(001) to $2.80\mu_B$. [Similarly, a moment of $2.92\mu_B$ on the Fe site is found for an Au/Fe/Au(001) sandwich.] However, when a monolayer of V(001) is sandwiched by Ag(001), the vanadium layer becomes paramagnetic. Apparently, the hybridization with Ag further reduces the LDOS of V near E_F and results in a Stoner factor which is just less than 1 (the exchange correlation parameter for V is 0.4 eV).[6]

The sensitivity of the magnetic ordering of V to its metallic environment is further illustrated by calculations with two layers of V on Ag(001): In this case the interface layer atoms remain essentially in the paramagnetic state and the surface layer has a moment of $1.15\mu_B$ which is substantially reduced from that of the single-overlayer value ($1.98\mu_B$). We thus have the result that a Ag substrate is more amenable for the magnetism of a V monolayer than is another V layer.

In Table I we also list the change of total energy due to spin polarization. In all cases, the magnetic state has a lower energy than that of the paramagnetic state. Moreover, we find that the effect of charge transfer is small—less than $0.1e$ from the noble to the transition metals—again reflecting their well-separated *d* bands.

There is a great wealth of other interesting possibilities. As illustration, we close with results of two such cases based on systems considered above: (i) For an overlayer of Cr on Fe/Au(001) the Cr moment is enhanced to $3.1\mu_B$ [which is smaller than the $3.7\mu_B$ for Cr on Au(001) but larger than the $2.49\mu_B$ for the surface layer of Cr(001)]. However, the Fe, now an interface layer, has its moment reduced to $-1.96\mu_B$ as a result of hybridization. (ii) For an overlayer of Fe on Cr/Ag(001), the Fe moment is reduced to $2.3\mu_B$ [i.e., smaller than either the value, $2.96\mu_B$, for Fe/Ag(001) or that for the surface layer of Fe(001), $2.98\mu_B$]. The interface Cr layer has a moment of $-2.4\mu_B$ which is larger than that of the Fe surface layer.

Work supported by the Office of Naval Research (Grant No. N00014-81-K-0438), the National Science Foundation (Grant No. DMR 82-16972 through the Northwestern University Materials Research Center), and a computing grant from the University of Minnesota. We are grateful to S. D. Bader and M. B. Brodsky for critical discussions and to J. H. Weaver for close cooperation and support.

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