Magnetism on the Surface of the Bulk Paramagnetic Intermetallic Compound YCo_2

S. Khmelevskyi,[1] P. Mohn,[1] J. Redinger,[1] and M. Weinert[2]

[1]*Institut für Allgemeine Physik and Center for Computational Materials Science, Vienna University of Technology, Getreidemarkt 9/134, A-1060 Vienna, Austria*

[2]*Department of Physics, University of Wisconsin - Milwaukee, P.O. Box 413, Milwaukee, Wisconsin 53201, USA*

(Received 13 October 2004; published 15 April 2005)

Using full-potential electronic structure calculations, we predict that the (111) surface of the cubic Laves phase Pauli paramagnet YCo_2 is ferromagnetic. The magnetism of the (111) surface is independent of the termination of the surface, does not extend beyond two Co layers, and is related to the field-induced metamagnetism of the bulk. YCo_2 appears to be a prominent candidate to demonstrate the phenomenon of surface-induced itinerant magnetism localized in two dimensions.

DOI: 10.1103/PhysRevLett.94.146403 PACS numbers: 71.20.Eh, 75.30.Kz, 75.70.Rf

Magnetic surfaces and multilayer systems continue to attract considerable interest both from a fundamental and an applied point of view. The reduced dimensionality in these systems gives rise to novel magnetic phenomena not observed in bulk materials. Artificially structured magnetic materials with reduced dimensionality are of major importance in current storage and sensor technology [1] and have led to revolutionary changes in many areas of microelectronics.

Because of its open d shell, isolated transition-metal ions possess large magnetic moments governed by Hund's rules. In bulk transition metals the crystal field quenches the free ion orbital momentum, and long-range magnetic order is observed only for the five metals in the middle of the $3d$ series, Fe, Co, Ni, Mn, and Cr. No intrinsic magnetic moments μ are detected for $4d$ or $5d$ metals and, with a few exceptions, only transition-metal alloys and intermetallic compounds of these five elements appear to be magnetic. The reduced coordination of atoms at surfaces of bulk systems or small clusters leads to smaller interactions among atoms and thus a narrowing of the local densities of states. The resulting electronic structures of the surface atoms approach the atomic limit where magnetism is favored. Intense studies of the surfaces and multilayer systems of magnetic transition metals have indeed confirmed such surface enhanced magnetism. In addition, the past two decades have witnessed a great deal of effort exploring new metallic materials that are nonmagnetic in the bulk but show intrinsic magnetic moments at the surface. A material with a magnetic surface and nonmagnetic bulk would be highly desirable for technological applications since thin films of such a material would provide a natural magnetic multilayer with perfect matching of the electronic potentials at the magnetic/nonmagnetic interface, thus preventing strong interface conduction electron scattering that normally arises.

One candidate that has attracted considerable theoretical and experimental interest is paramagnetic bcc V where a large peak in the electronic density of states (DOS) near the Fermi level suggests that it is very close to the onset of the magnetic ordering [2]. Although electron-capture spectroscopy measurements [3] have been interpreted as indicating magnetic ordering in the topmost layer of V(100) up to 540 K, calculations predict a paramagnetic surface [4] and, to the best of our knowledge, no further experimental evidence of the magnetism of the V(100) surface is available. Since nonmagnetic surfaces were also predicted for other strongly exchange-enhanced paramagnetic transition metals such as Rh [5] and Pd [6], the interest shifted to magnetism induced by effects of low dimensionality of V or $4d$ and $5d$ mono- and multilayers deposited on the surfaces of noble metals [7,8] or Fe [9] where the appearance of magnetism was theoretically predicted and unambiguously verified experimentally [10]. Continuing the search for paramagnetic metallic materials with magnetic surfaces, the calculations of Turek *et al.* [11] predicted magnetism for the surfaces of paramagnetic disordered bcc PdV, RuV, and RhV alloys over a wide composition range. These structures, however, may be very hard to realize experimentally since these disordered alloys are expected to segregate at the surface [12], which in turn would suppress the surface magnetism.

In this Letter we present a first-principles density functional theory (DFT) investigation of the stable (111) surface of the paramagnetic intermetallic compound YCo_2, crystallizing in the cubic Laves (C15) structure (Fig. 1). Our calculations demonstrate that bulk paramagnetic YCo_2 becomes ferromagnetic at the surface with large magnetic moments in the topmost Co layer for both Y- and Co-terminated (111) surfaces. This stoichiometric compound was chosen as a promising candidate to show surface-induced magnetism because of its rather peculiar bulk magnetic properties. YCo_2 is known to be a strongly exchange-enhanced Pauli paramagnet that at low temperature exhibits a first-order metamagnetic phase transition into a magnetically ordered state at an applied magnetic field of about 70 T [13]. This phenomenon, known as itinerant electron metamagnetism (IEM), was first predicted by Rhodes and Wohlfarth [14] and then experimentally observed in YCo_2-based alloys. Various unusual phenomena related to the IEM instability of the Co sublattice in bulk RCo_2 ($R =$ rare earth atoms) intermetallics

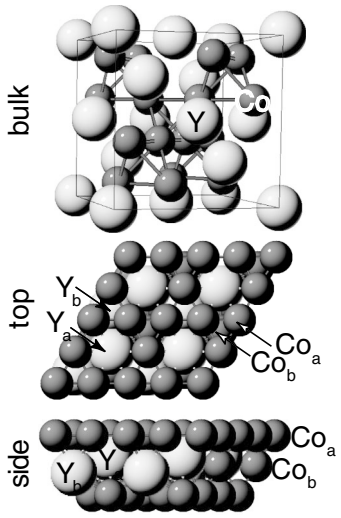

FIG. 1. Structure of the cubic Laves phase (C15) compound YCo_2: upper panel: bulk. Lower panels: top and side view of the Co-terminated $YCo_2(111)$ surface. *a, b* denote different Y and Co sites introduced by the surface.

and related alloys have been studied starting from the middle 1960s up to the present [15,16]. Of these various alloys, YCo_2 is closest to a magnetic instability, as illustrated by the weak itinerant magnetism found in $Y(Co, Al)_2$ [17] where substitution of 12% nonmagnetic Al for Co causes disorder-induced changes in the Co density of states [18] that trigger the magnetic instability.

In addition, YCo_2 is interesting because (i) the low index planes of the C15 Laves structure contain atoms of only one kind (see Fig. 1), so a surface of either pure Y or Co is possible; (ii) the $YCo_2(111)$ Co-terminated surface is latticed matched to Cu(111), which may eventually allow the use of magnetically ''dead'' Cu cap layers; and (iii) epitaxial multilayer films of cubic Laves phase $YCo_2(111)$ were successfully grown on a bcc W(110) surface [19] and confirm the stability of a $YCo_2(111)$ surface with no significant lateral reconstructions. Unfortunately, no magnetic studies of this system were reported [20].

The electronic structure was calculated employing the full-potential linearized augmented plane wave method (FLAPW) as embodied in the FLAIR code [21,22]. Exchange and correlation are treated within the local spin-density approximation (LSDA) using the Perdew-Zunger (Ceperly-Alder) parametrization [23]. In agreement with experiment, bulk YCo_2 is nonmagnetic at the calculated equilibrium lattice constant ($a = 6.957$ Å). The surface electronic structure was simulated using a repeated periodic slab geometry (for details, see Ref. [24]) with up to 27 layers of Y and Co. At the center of the slab the local atomic DOS for both Co and Y are found to be essentially identical to those from a bulk calculation, suggesting that our slab geometry reliably models the corresponding surface and bulk material for both Co- and Y-terminated (111) surfaces of YCo_2.

Before considering the surface magnetism, we briefly discuss the bulk magnetic properties of YCo_2. At the experimental lattice constant, the LSDA predicts a magnetic state with $\mu \sim 3.4\mu_B$ per (6-atom) unit cell, while at the smaller LSDA lattice constant the system is nonmagnetic. [The generalized gradient approximation (GGA) has a larger equilibrium volume and a magnetic ground state, contrary to experiment.] Within the fixed spin moment (FSM) approach, the separation between the Fermi levels of the two spin directions allows us to determine the magnetic field necessary to maintain a given moment; the results for μ vs applied field (H) are shown in Fig. 2. At low fields, YCo_2 shows paramagnetic behavior, although the susceptibility is strongly dependent on the lattice constant, reflecting the growing tendency toward magnetism with increasing lattice constant. For larger H, there is a rapid rise in μ and, importantly, the curve is not monotonic. The existence of multiple solutions (different moments) at a single field is the signature of the IEM. At the calculated LSDA lattice constant, the required field for multiple solutions is several hundred teslas and the moments per Co are small. At a slightly expanded lattice constant of 7.086 Å, there are multiple solutions for $H \sim 60$ T ($\sim 0.5\mu_B$ and $\sim 0.07\mu_B$/Co). To determine which solution is the stable one, we need to compare the (Legendre-transformed) free energies at *constant field*, as shown in the inset to Fig. 2. The low moment (paramagnetic regime) is stable until a field of about 100 T, at which point the high-moment solution of $2.5\mu_B$/unit cell, or about $0.73\mu_B$/Co atom, is stable, in reasonable agreement with experiment [13]. (Each Y has $\mu \sim -0.2\mu_B$.) LSDA is thus capable of qualitatively describing the underlying complicated magnetic properties. It should be noted that a description of IEM within LSDA neglects the effects of magnetic zero-point fluctuations (ZPF) [25]. However, renormalization of LSDA-FSM energies due ZPF even enhances magnetism and thus lowers the critical field

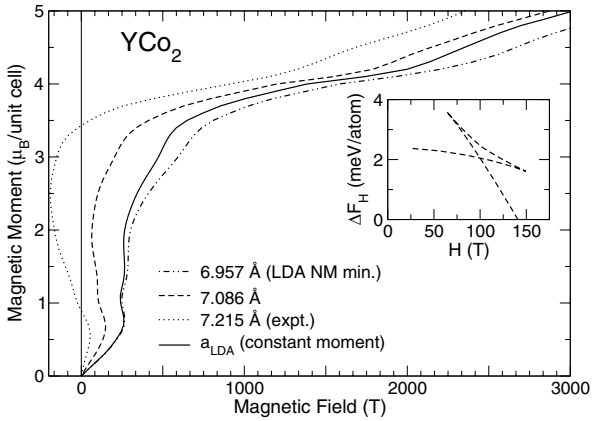

FIG. 2. Calculated magnetic moment vs applied field for bulk YCo_2 at lattice constants corresponding to equilibrium nonmagnetic LDA, to experiment, to a value halfway between, and to the calculated equilibrium values determined for fixed μ. The inset shows the relative free energy at constant magnetic field for $a = 7.086$ Å. (Note that only comparisons of ΔF_H at the *same* field are meaningful.)

[26], so that its overestimation by LSDA is fully consistent with the predictions from ZPF theory.

For both Y- and Co-terminated surfaces, the topmost Co layers are calculated (in zero field) to be magnetic. For the unrelaxed Co-terminated surface, the surface (second layer) Co has a moment of $1.33(0.60)\mu_B$/Co and close to zero for the rest of the layers. To obtain a more realistic description of the atomic arrangement we also allowed for the full relaxation of the atoms in the outer six layers by minimizing the atomic forces. Despite a rather large contraction of the top Co-Y interlayer distance, which suppresses magnetism, we find the same magnetic situation at the surface, albeit with a slightly reduced surface moment of $1.05\mu_B$/Co. For the Y-capped surface, interlayer relaxations are rather moderate, whereas intralayer relaxations are negligible for both surfaces. The calculated moments in the Co and Y layers are presented in Table I.

Several observations can be made: (i) the second Co layer for the Co-terminated surface is magnetic despite the fact that it has the same nearest neighbor atomic environment as in the bulk. The value of the moment, however, is strongly reduced compared to that of the surface layer. At the same time, this value corresponds to that observed in bulk YCo_2 for magnetic fields higher than the critical value for the IEM of 70 T [13]. This suggests that the magnetism in the second Co layer is induced by the field of the surface Co layer; i.e., we are observing an IEM transition in an essentially two-dimensional system. (ii) In the case of Y termination only the first Co layer is intrinsically magnetic, but with a reduced magnetic moment of $0.79\mu_B$/Co. Consequently, due to the reduced moment of the surface Co layer, the IEM transition in the adjacent Co layer is no longer observed. This fact may have technological importance since the appearance of surface magnetism in this system appears to be fairly independent of the details of the termination or growth process. (iii) Deeper into the slab, the small alternating Co and Y magnetic moments, reflecting the oscillatory nature of magnetic interactions in metals arising from the polarization of the conduction electrons by the magnetic surface Co layer, are strongly damped with distance from the surface. (iv) Similarly, the small induced antiparallel moments in Y are due to spin-polarization effects, also seen in bulk YCo_2 in the metastable high-moment state [27], in YFe_2 and $ZrFe_2$ [28], and in magnetic heavy rare earths RCo_2 compounds with ferrimagnetic order of the R and Co sublattices [15].

To verify the robustness of the surface magnetism, we considered the interplay of spin polarization, different terminations, and structural relaxations. Inspection of the surface bands does not suggest any strong Fermi surface driving force (nesting) for reconstructions. The surface moments remain stable irrespective of the termination, which (based on total energy calculations) is most likely Y. Even a Cu termination does not kill the Co moments at the interface, which remain at about $0.9\mu_B$/Co. Thus, possible reconstructions might slightly alter the values of the Co moments at the surface or below, but not the overall picture. Similarly, relaxations and volume effects are not the cause of the surface magnetism. The atomic volume for Co at the Y-terminated surface is approximately the same as that in the bulk, and significantly smaller than the volume required to have bulk magnetism. (Because the LSDA underestimates the equilibrium volume, the absolute values of the relaxations in Table I are likely too small, but fractional ones generally are described much better.)

As shown above, bulk YCo_2 is near a metamagnetic transition. Not too surprisingly, other effects besides an applied field may drive (parts of) the system magnetic. The formation of the surface magnetic moments in YCo_2 can be understood already within the itinerant picture of magnetism on the basis of the calculated nonmagnetic DOS. In Fig. 3 the atom-resolved non-spin-polarized Co DOS for various layers are shown. For the surface Co layer, the Fermi energy ε_F intersects at the top of the Co d band with a DOS large enough to fulfill the Stoner criterion for the onset of magnetism. This increase of the surface DOS at ε_F

TABLE I. Layer resolved magnetic moments μ_i and interlayer distances $d_{i,i+1}$ in Å for $YCo_2(111)$ surfaces. The $\Delta d_{i,i+1}$'s denote deviations in Å from the unrelaxed calculated bulk equilibrium values. The numbering of the layers starts at the surface Co layer (layer 1) which may be capped with one Y cap layer (layer 0). Subscripts *a, b* label different sites as depicted in Fig. 1

Layer	Atom	Co-terminated Unrelaxed		Co-terminated Relaxed		Y-capped Relaxed	
i	Type	μ_i	$d_{i,i+1}$	μ_i	$\Delta d_{i,i+1}$	μ_i	$\Delta d_{i,i+1}$
0	Y cap	⋯	⋯	⋯	⋯	−0.12	0.02
1	Co_a	1.33	1.51	1.05	−0.35	0.79	−0.01
2	Y_a	−0.14	0.50	−0.13	0.28	−0.06	−0.02
3	Co_b	0.60	0.50	0.62	−0.05	0.05	0.03
4	Y_b	−0.09	1.51	−0.09	−0.10	−0.02	−0.04
5	Co_a	0.01	1.51	0.09	0.00	−0.14	0.00
6	Y_a	−0.01	0.50	−0.02	−0.04	0.01	−0.01
7	Co_b	0.04	0.50	0.21	0.00	−0.05	0.00
8	Y_b	−0.01	1.51	−0.02	0.00	0.01	0.00
9	Co_a	0.01	1.51	0.05	0.00	0.02	0.00

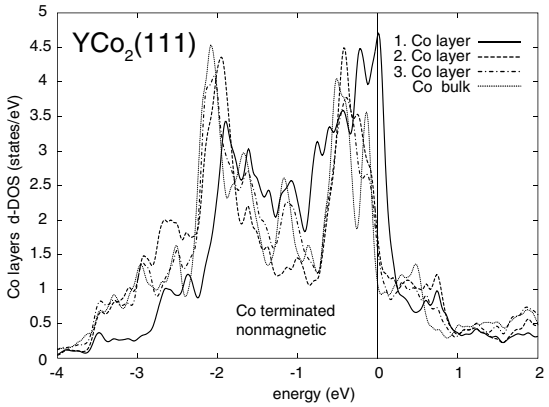

FIG. 3. Nonmagnetic DOS for a bulk-truncated unrelaxed Co-terminated $YCo_2(111)$ surface.

is due to the reduced coordination number, which results in the well known band narrowing at the surface and subsequent shift of the *d* states to maintain charge neutrality; for this almost filled *d* band, the shift is to higher energy. Already by the third Co layer the DOS is largely bulklike and the DOS is too small to fulfill the Stoner criterion. Magnetic ZPF provide an additional mechanism that would serve to further enhance the tendency towards magnetism.

Our results predict the existence of a stable magnetic (111) surface of the intermetallic compound YCo_2 which otherwise is nonmagnetic in the bulk. The magnetism of this surface is connected with the field-induced metamagnetism of the bulk. The thickness of the magnetic region does not exceed the two top Co layers and is independent of the surface termination. This new magnetic feature may provide an opportunity to study itinerant magnetism and itinerant metamagnetic phenomena localized in two dimensions, using highly sensitive modern experimental methods for surface electronic structure analysis.

[1] Special issue on Magnetism Beyond 2000, edited by A. J. Freeman and S. D. Bader [J. Magn. Magn. Mater. **200** (1999)].
[2] T. M. Hattox, J. B. Conklin, Jr., J. C. Slater, and S. B. Trickey, J. Phys. Chem. Solids **34**, 1627 (1973).
[3] C. Rau, C. Liu, A. Schmalzbauer, and G. Xing, Phys. Rev. Lett. **57**, 2311 (1986).
[4] S. Ohnishi, C. L. Fu, and A. J. Freeman, J. Magn. Magn. Mater. **50**, 161 (1985).
[5] M. Weinert, S. Blügel, and P. J. Johnson, Phys. Rev. Lett. **71**, 4097 (1993); J.-H. Cho and M. Scheffler, Phys. Rev. Lett. **78**, 1299 (1997).
[6] S. Blügel, Europhys. Lett. **18**, 257 (1992).
[7] H. Beckmann, Fei Ye, and G. Bergmann, Phys. Rev. Lett. **73**, 1715 (1994).
[8] J. Redinger, S. Blügel, and R. Podloucky, Phys. Rev. B **51**, 13852 (1995).
[9] T. G. Walker and H. Hopster, Phys. Rev. B **49**, 7687 (1994).
[10] D. Spišák and J. Hafner, Phys. Rev. B **61**, 4160 (2000).
[11] I. Turek, S. Blügel, and J. Kudrnovsky, Phys. Rev. B **57**, R11065 (1998).
[12] A. V. Ponomareva, L. V. Pourovskii, E. I. Isaev, Yu. Kh. Vekilov, B. Johansson, and I. A. Abrikosov, J. Magn. Magn. Mater. **258-259**, 128 (2003).
[13] T. Goto, T. Sakakibara, K. Murata, and H. Komatsu, Solid State Commun. **72**, 945 (1989).
[14] E. P. Wohlfarth and P. Rhodes, Philos. Mag. **7**, 1817 (1962).
[15] N. H. Duc and T. Goto, in *Handbook on Physics and Chemistry of Rare-Earths*, edited by K. A. Gschneider and L. Eyring (North-Holland, Amsterdam, 1999), Vol. 26, Chap. 171, p. 177.
[16] N. H. Duc and P. E. Brommer, in *Handbook on Magnetic Materials*, edited by K. H. J. Buschow (North-Holland, Amsterdam, 1999), Vol. 12, Chap. 3.
[17] K. Yoshimura and Y. Nakamura, Solid State Commun. **56**, 767 (1985).
[18] S. Khmelevskyi, I. Turek, and P. Mohn, J. Phys. Condens. Matter **13**, 8405 (2001).
[19] F. Robaut, S. Jaren, N. Cherief-Benbrahim, and C. Meyer, Appl. Phys. Lett. **69**, 1643 (1996).
[20] Only transverse magneto-optical Kerr effect studies of $YCo_2/GdCo_2/YCo_2$ thin films have been reported [H. Salas *et al.*, J. Phys. II (France) **4-8**, 277 (1998)].
[21] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B **24**, 864 (1981); H. J. F. Jansen and A. J. Freeman, *ibid.* **30**, 561 (1984).
[22] Michael Weinert, FLAIR, http://www.uwm.edu/~weinert/flair.html.
[23] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981); D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[24] Well converged results were obtained for plane wave cutoff of $k_{\max} = 4.0$ a.u.$^{-1}$. Inside the spheres, the angular momentum expansion was taken up to $\ell_{\max} = 8$, for both the wave functions and the full-potential/charge density representation. The core electrons, including the $4p$ states for Y, were treated fully relativistically and the valence electrons scalar relativistically. The in-plane lattice constants were fixed at the corresponding calculated bulk values leading to a Co-Co distance of 2.46 Å only slightly larger than the 2.43 Å obtained for close-packed Co. The calculations employ a vacuum layer of ≈11.5 Å separating the slabs, a centered *k* mesh of 4 special points in the irreducible wedge of the corresponding two-dimensional Brillouin zone for geometry calculations, and a *k* mesh of 19 special points in the final step including the calculation of magnetic moments and the DOS. For the bulk calculations, 72 *k* points in the irreducible wedge were used.
[25] A. Z. Solontsov and D. Wagner, Phys. Rev. B **51**, 12410 (1995).
[26] S. Hirooka, J. Phys. Condens. Matter **12**, 5669 (2000).
[27] P. Mohn and K. Schwarz, J. Magn. Magn. Mater. **104-107**, 685 (1992).
[28] P. Mohn and K. Schwarz, Physica B (Amsterdam) **130**, 26 (1985).