

YCo₂: Intrinsic Magnetic Surface of a Paramagnetic Bulk Material

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Here we report on results of a spin-resolved photoelectron spectroscopic (SRPES) study of YCo₂ thin films (150 Å-thick) grown on a W(110) substrate. The films were prepared by co-deposition of stoichiometric amounts of Y and Co onto a clean W surface followed by thermal annealing leading to (2 × 2) overstructure with respect to W(110) in the low-energy electron diffraction pattern indicated formation of a structurally ordered YCo₂(111) surface. While no clear spin asymmetry was observed for bulk-sensitive SRPES data taken at $h\nu = 1253.6$ eV, the more surface-sensitive SRPES data obtained at $h\nu = 21.2$ eV photon energy revealed a clear spin-asymmetry probing the validity of the recent theoretical prediction.

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Two-dimensional magnetism has attracted considerable interest during the last decades. In nature, respective systems might be realized in layered compounds, thin films, or artificial multilayers. Particularly fascinating is the idea of a magnetically ordered surface on top of a nonmagnetic solid since it represents an intrinsic property of the respective material that may be important for many interactions in physics, chemistry, and biology. Surface magnetism may be caused by the reduced atomic coordination at the surface that leads to band narrowing and in some cases to valence transitions, partial lifting of the quenching of orbital momentum, and changes of crystallographic structure and chemical composition at the surface.

The question of whether the reduced dimensionality at the surface may modify the electronic structure of a paramagnetic material in a way that it becomes intrinsically magnetic near the surface but stays paramagnetic in the bulk has attracted considerable attention in the past [1–4]. The general possibility to achieve such a situation follows from the well-known facts that the reduced coordination at the surface leads to band narrowing of the metallic bands and creation of surface states that eventually enhance the density of states at the Fermi level. This might lead to magnetic instabilities as predicted by established theories of itinerant magnetism [5]. Apart from the density of states, also the magnitude of local magnetic moments may change at the surface: in the case of rare earth systems, surface energy shifts of $4f$ states may lead to valence transitions and drastic changes of the magnetic properties [6]. In transition-metal systems, the quenching of angular momentum becomes partially lifted leading together with an altered occupation of d orbitals to local magnetic moments that may differ considerably from those of the bulk.

The search for such surface induced magnetism was directed quite naturally to the paramagnetic transition metals with an open d shell, which exhibit a strongly enhanced paramagnetic susceptibility in the bulk, like vanadium [1] or rhodium and palladium [2] and their alloys [7]. However, the existence of magnetic surfaces for these materials was neither confirmed experimentally [8] nor on the basis of first-principles calculations [9–11]. Magnetism is found only for thin films of V and Rh on a magnetic substrate like Fe, where magnetic order is induced by the substrate [12,13].

Starting from the fact that genuine magnets like Co and Ni often lose their magnetism in bulk intermetallic compounds [14], one could hope that for some of them magnetism could be restored in the surface region. In fact, surface magnetism was reported recently [15] for CoAl where it is caused, however, by a change of stoichiometry at the surface and not by a simple breaking of bonds alone. We explore the possibility of the latter for the strongly enhanced Pauli paramagnet YCo₂ (cubic Laves phase), which was the first material where the phenomenon of itinerant electron metamagnetism predicted 40 years ago by Rhodes and Wohlfahrt [16] was observed [17]. Applying a high magnetic field (70 T) a first order magnetic phase transition takes place [17], which confirms its proximity to a ferromagnetic instability. Furthermore, Co atoms become magnetic upon alloying with nonmagnetic Al, by replacing Y with a magnetic rare earth element [18], or by inducing a structural disorder like amorphization [19]. These facts, together with recent theoretical predictions about a possible magnetic instability of its surface [20], make YCo₂ an ideal candidate to probe surface induced magnetism.

In this contribution, we report for the first time on the unambiguous experimental observation of the formation of magnetic order of the surface of bulk paramagnetic compound YCo_2 by means of spin-resolved photoemission. Taking advantage from variation of the surface sensitivity of the method as a function of photon energy allowed us to discriminate spectral contributions from bulk and surface. The results demonstrate that the $\text{YCo}_2(111)$ surface is intrinsic magnetically ordered, whereas the bulk remains nonmagnetic, confirming a recent theoretical prediction [20] that such a situation might occur in this metamagnetic material.

Spin-resolved photoelectron spectra were collected in an angle-integrated mode with a 180° hemispherical energy analyzer SPECS PHOIBOS 150 combined with a 25 kV Mott detector for spin analysis [21]. The energy resolution of the analyzer was set to 100 and 500 meV for ultraviolet photoelectron spectroscopy and x-ray photoelectron spectroscopy, respectively. The incident angle of the light was 30° with respect to the sample surface, and the photoelectrons were collected around surface normal. Spin-resolved measurements were performed in magnetic remanence after having applied a magnetic field pulse of about 700 Oe along the in-plane $\langle 1\bar{1}0 \rangle$ axis of the W(110) substrate. The experimental setup asymmetry was accounted for in the standard way by measuring spin-resolved spectra for two opposite directions of applied magnetic field [22]. Thick YCo_2 films, with a thickness of 150 Å as monitored by a quartz microbalance, were grown epitaxially on W(110) (as proposed in work [23]) at RT by co-deposition of high-purity Y and Co metals (ratio for deposition rates was Y: Co = 1 ML/min:2 ML/min) from carefully degassed electron-beam evaporators. Subsequent annealing at 300°C leads to a well-ordered $\text{YCo}_2(111)$ surface as indicated by a sharp hexagonally ordered LEED pattern (Fig. 1). Hereby, the $\langle 1\bar{1}2 \rangle$ direction of the fcc YCo_2 lattice [Fig. 1(a)] is found to lie parallel to the dense row $\langle \bar{1}1\bar{1} \rangle$ of the W substrate as shown in the right upper corner of Fig. 1(b). Kinematic LEED simulations as well as ones by means of the LEEDpat2-software [24] confirm the validity of this model. Quantitative analysis of photoelectron core-level spectra confirmed the expected stoichiometries of YCo_2 thick films to within experimental accuracy and further showed minimal degrees of surface stoichiometry alteration (within $\pm 5\%$ for both species) or surface contamination (e.g., less than 0.1 monolayers of oxygen or carbon contaminant) during experiment.

LSDA calculations, which support our experimental observations, were performed at the calculated nonmagnetic bulk equilibrium lattice constant ($a = 6.957 \text{ \AA}$) using the full-potential linear augmented plane wave method as implemented in the FLAIR code [25]. Well-converged results could be obtained for a plane wave cutoff $k_{\text{max}} = 4.0$ a.u. and an angular momentum expansion up to $\ell_{\text{max}} = 8$, both for the full-potential and charge-density representation inside the muffin-tin spheres. In contrast to

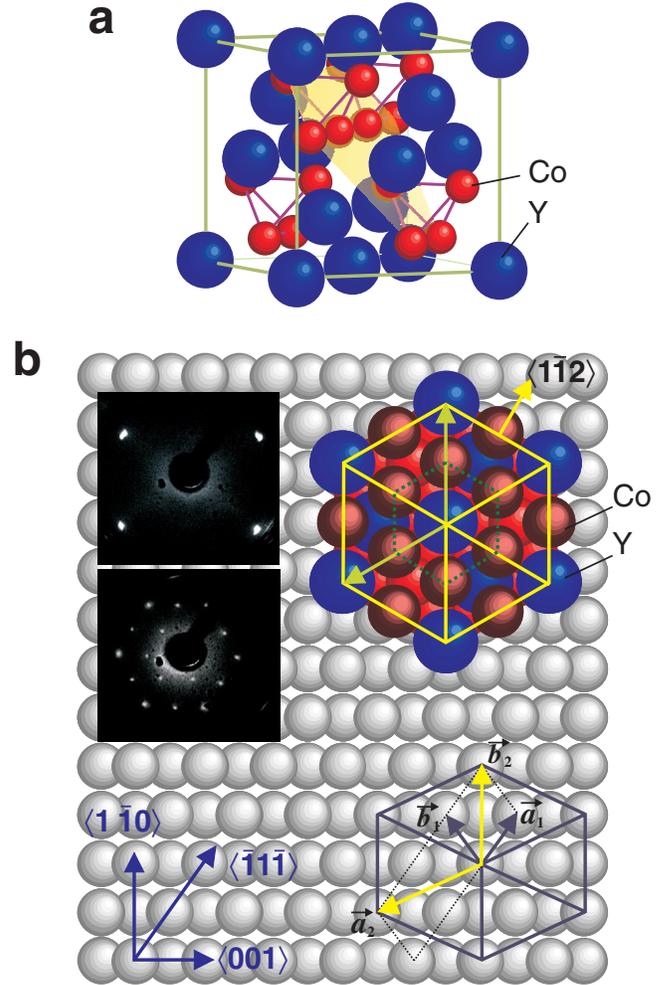


FIG. 1 (color online). Crystallographic structure of $\text{YCo}_2(111)$ surface. (a) The YCo_2 bulk unit cell. Large and small spheres are Y and Co atoms, respectively. Shaded plane means (111) surface. (b) Growth model of the $\text{YCo}_2(111)$ epitaxial film on top of the W(110) single crystal. Inset shows the low-energy electron diffraction spots obtained on clean W(110) surface (upper LEED image) and 150 Å-thick $\text{YCo}_2(111)$ film (bottom LEED image). Observed LEED image is clear from the following consideration of the crystallographic structure of the $\text{YCo}_2(111)/\text{W}(110)$ system. The distorted hexagon in the right lower corner of Fig. 1(b) is formed on the basis of unit cell of the W(110) surface (the unit vectors of this cell are marked by dark arrows: \vec{a}_1 and \vec{b}_1). The bright vectors (\vec{a}_2 and \vec{b}_2), obtained by transformation from W(110)-unit cell's vectors, can be transformed to the unit vectors of the hexagonal cell of $\text{YCo}_2(111)$ surface by slight distortion [mainly in $\langle 1\bar{1}0 \rangle$ direction of the W(110) surface]. The resulted structure of the $\text{YCo}_2(111)$ surface together with hexagonal unit cell and unit vectors (bright hexagon and arrows) is shown in the right upper corner. The presented crystallographic structure was also confirmed by LEED simulation performed by LEEDpat2 package [24].

the fully relativistic treatment of core electrons, spin-orbit coupling for the valence electrons is dropped. The surface electronic structure was calculated using a repeated peri-

odic slab geometry with up to 25 (27 with Y cap) layers of Y and Co atoms per slab separating the slabs by vacuum layers of ≈ 12 Å thickness. Atoms in the outer 6 layers were allowed to find their optimum geometry by minimizing the atomic forces.

Spin-resolved photoelectron experiments were performed in angle-integrated mode probing the valence-band density of states (VB-DOS) with two different photon energies: $h\nu = 21.2$ eV and 1253.6 eV. For the valence-band spectra, the escape depth of the photoelectrons varies approximately from 7 Å ($h\nu = 21.2$ eV) to 25 Å ($h\nu = 1253.6$ eV), as can be estimated from the universal curve for inelastic mean free path [26], allowing for a proper separation of surface- and bulk-derived phenomena. Spin-resolved spectra (up and down triangles for spin-up and spin-down intensities, respectively) and the corresponding spin polarizations (filled symbols) as functions of binding energy are shown in Fig. 2(a) and 2(b) for $h\nu = 1253.6$ eV and 21.2 eV, respectively. The spin polarization is determined by $P = (N_{\uparrow} - N_{\downarrow}) / (N_{\uparrow} + N_{\downarrow})$, where N_{\uparrow} and N_{\downarrow} are the numbers of spin-up and spin-down electrons in the valence band as determined by spin-resolved measurements in magnetic remanence after having applied a magnetic field pulse. The spectra measured with higher surface sensitivity ($h\nu = 21.2$ eV) show a clear spin asymmetry, which is lost in the bulk-sensitive spectra ($h\nu = 1253.6$ eV). These results demonstrate for the first time unambiguously the presence of magnetic order on a surface of an intrinsically nonmagnetic bulk material. For comparison in the lower panels of Fig. 2(a) and 2(b) the spin-polarization curves for Co(0001) thin films (open symbols) are presented. In case of the $h\nu = 21.2$ eV photon energy the corresponding spin-polarization values for Co film were reduced by factor of 2.

In order to discuss observed phenomenon of surface ferromagnetic order of paramagnetic bulk material theoretically, we performed *ab initio* band structure calculations for the stable (111) surface of the paramagnetic intermetallic compound YCo_2 [20] using the full-potential linear augmented plane wave method [27,28] and the local spin density approximation (LSDA) for treating exchange and correlation [29]. Taking the bonding energy of an additional Co or Y layer as a measure, the results for relaxed Co- and Y-surface terminations clearly show that a Y-terminated surface is energetically favored. For both terminations the Co atoms at the surface are magnetic with corresponding moments of $1.05\mu_B$ and $0.79\mu_B$, respectively, thus being almost independent of the termination of the surface. These values are close to the Co moments in bulk YCo_2 above the metamagnetic transition [17]. For the bulk, our calculations yield a paramagnetic ground state with essentially zero Co moments for the third Co layer and below. In Fig. 2(c) we present the results of our spin-resolved slab calculations. The left-hand panel shows the spin-resolved Co layer projected DOS for bulk YCo_2 (shaded area as a background) as compared to the respec-

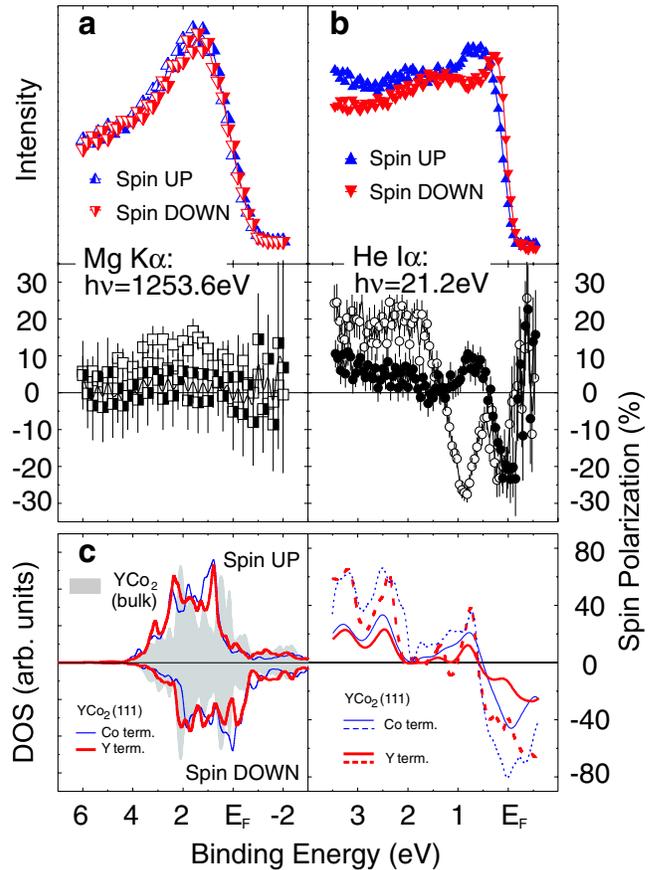


FIG. 2 (color online). Manifestation of the surface magnetism of YCo_2 . (a) Bulk-sensitive spin-resolved photoelectron spectrum and corresponding spin polarization (filled symbols) of YCo_2 obtained at $h\nu = 1253.6$ eV of photon energy. (b) Surface-sensitive spin-resolved spectrum and corresponding spin polarization (filled circles) of the $\text{YCo}_2(111)$ surface obtained at $h\nu = 21.2$ eV demonstrates clear spin asymmetry. The spin-polarization curves for Co(0001) thin films (open symbols) are presented here for comparison by open symbols. In case of the $h\nu = 21.2$ eV photon energy the corresponding spin-polarization values for Co film were reduced by factor of 2. (c) Left: results of spin-polarized slab calculations show spin-resolved density of states of central-slab Co atom by dashed area, and ones of Co surface layer for relaxed Co- (thin lines) as well as Y-terminated (thick lines) of $\text{YCo}_2(111)$ surface. Right: corresponding spin polarizations calculated as normalized difference of spin-up and spin-down DOSs are shown for these two terminations by dashed lines with respective thickness. The resulting spin polarizations after taking into account the photoelectron escape depth (that leads to the reduction of corresponding contributions from

tive DOS of the two possible terminations of the $\text{YCo}_2(111)$ surface: relaxed Co (thin blue line) as well as relaxed Y termination (thick red line). In the right-hand panel the corresponding spin polarizations calculated as normalized difference of spin-up and spin-down DOSs are shown for these two terminations by dashed lines with respective thickness. The resulting spin polarizations after taking into account the photoelectron escape depth (that leads to the reduction of corresponding contributions from

subsurface Co and Y layers) are shown by solid lines. In our analysis we use only the Co projected DOS since the Co 3d photoelectron cross section at 21.2 eV photon energy is much larger than the one of the Y 4d states and the VB-DOS in the vicinity of Fermi level consist mainly of Co 3d electrons [18]. The surface-sensitive spin-resolved PE data photoemission are in very good agreement with both the calculated DOS as well as the shape of the spin-polarization curve around the Fermi energy. The main features are presented in both calculated and measured spectra. From the fact that we observe a clear manifestation of the ferromagnetic ordering of the YCo₂(111) surface at room temperature, it follows that the Curie temperature of the magnetically ordered YCo₂(111) surface is higher than 300 K. If we assign two peaks of the experimental spectra: spin-up and spin-down features at about 0.69 (spin-up) and 0.29 eV (spin-down) binding energy, respectively, to the exchange spin splitting and use the empirical proportionality of 1 eV/1 μ_B between the value of splitting and the magnetic moment for 3d electrons [30], we arrive at a value of 0.4 μ_B /Co atom from the experimental data, which is approximately by a factor 2 smaller as compared to the calculated one for both Co and Y terminations. The shape of the spin polarization as a function of binding energy calculated from first principles presented in Fig. 2(c) (right panel) is in good agreement with the measured one [Fig. 2(b), for both Co- and Y-terminated surfaces of YCo₂]. The quantitative difference may be attributed to the final temperature in our experiment, or to final escape depth of photoelectrons and that photoemission signal contains also nonvanishing contributions from deeper layers.

In summary, our spin-resolved photoelectron spectra show unambiguously that the Co atoms in the (111) surface layers of the intermetallic compound YCo₂ are magnetically ordered, whereas the signal from the bulk lacks any spin polarization. This result is in perfect agreement with earlier theoretical predictions based on first-principles calculations [20]. Our finding is not only of interest for the basic understanding of low dimensional magnetic ordering, but it also provides a new prospect of the application of materials which show the long known effect of itinerant electron metamagnetism. These results also offer an obvious potential for technological application as these systems possess a naturally occurring ideal magnetic-nonmagnetic interface. Such an ideal interface reduces unwanted scattering of conduction electrons in possible electronic applications. Moreover, the preparation of such a naturally occurring magnetic layer becomes much more simple and attractive since magnetic order is an intrinsic property of the clean sample surface.

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