Observation of ferromagnetic surface of paramagnetic YCo$_2$

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Abstract. Here we present results on the experimental observation of intrinsic surface magnetism of the bulk paramagnetic material YCo$_2$. As predicted by theory, the observed magnetism of the low-index crystallographic (111) plane of YCo$_2$ is explained by the increasing of density of electronic states at the Fermi level due to the reduced atomic coordination at the surface. Since this magnetic order exists at room temperature, YCo$_2$ shows great potential for an application in magnetic nanotechnology.

The question whether the effects of reduced dimensionality on the surface can modify an electronic structure of paramagnetic metallic material in a way that it becomes intrinsically magnetic near the surface and stay paramagnetic deeper in the bulk have attracted a considerable attention in the past. The principal possibility to achieve such situation follows from the well-known facts that surface effects might change the electronic structure of material, e.g., leading to the narrowing of the metallic bands and creation of the localized surface states and therefore to eventual enhancement of the number of electronic states with maximal Fermi energy. This might lead to the magnetic instability predicted by simple itinerant theories of magnetism (for example, Stoner theory stays that transition from paramagnetic to ferromagnetic state becomes favorable if $D(E_F) \cdot I > 1$, where $D(E_F)$ is the density of states (DOS) at the Fermi level ($E_F$) and $I$ is an atomic exchange integral [1]). The search for such surface induced magnetism was directed quite naturally to the paramagnetic 3$d$- and 5$d$-transition metals elements. Main candidate was V (also Rh, Pt, Pd and their alloys) which exhibits a strongly enhanced paramagnetic susceptibility in the bulk [2-4]. The existence of magnetic surfaces on them were not confirmed neither experimentally [5] nor predicted on the basis of full-potential calculations [5-7]; the only magnetic multilayers of V and Rh was observed on magnetic substrate like Fe, where the magnetism is induced by the substrate and thus being not intrinsic [8,9].

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Figure 1. Upper part shows LEED images of (a) pure W(110) and (b) YCo$_2$(111) surfaces. Lower part demonstrates the crystallographic structure of the YCo$_2$(111)/W(110) system: large and small spheres are Y and Co atoms, respectively (see explanation of growth mode in the text).

It is known, however, that certain magnetic metals like Co and Ni might become non-magnetic in intermetallic compounds [10]. Thus, one may expect that in some of them the magnetism of 3d-element can be recovered due to presence of the surface, but remain non-magnetic in the bulk. We have chosen for our study a paramagnetic YCo$_2$ compound, since it is strongly enhanced Pauli paramagnet and being very close to the ferromagnetic instability what manifests itself in first order phase transition to magnetic state if extremely high magnetic field is applied (70 T) [11]. Generally, it was a first material where the phenomena of itinerant electron metamagnetism (IEM) transition predicted 40 years ago by Rhodes and Wholfarth was observed [12]. In this material Co-atoms might be turn on to be magnetic by alloying with non-magnetic Al, placing a magnetic rare earth (RE) element instead of Y, or by inducing a structural disorder making it amorphous [13,14]. These facts, together with recent theoretical predictions about ferromagnetic ordering of YCo$_2$(111) surface [15], make it an ideal candidate to show a phenomena of surface induced magnetism.

To proof this prediction we have chosen photoelectron spectroscopy, since sensitivity of this method from surface-to-bulk can be varied as a function of photon energy used. Here, we report the first unambiguous experimental observation of the formation of magnetic surface on top of paramagnetic bulk in the same sample: by using spin-polarized photoemission in both the ultraviolet (UPS) and the x-ray (XPS) regimes, we are able to separately probe the surface and the bulk, respectively, of YCo$_2$(111). The results demonstrate that the YCo$_2$(111) surface is intrinsically magnetic, whereas the bulk remains non-magnetic, confirming a recent theoretical prediction that such a situation might occur in these itinerant electron metamagnetic materials [15].

Spin-resolved photoelectron spectra (He I$\alpha$, $h\nu = 21.2$ eV and Mg K$\alpha$, $h\nu = 1253.6$ eV) were recorded at room temperature (RT) in angle-integrated mode with a 180° hemispherical energy analyzer SPECS PHOIBOS 150 combined with a 25 kV Mott detector for spin analysis. The energy resolution of hemispherical analyzer was set to 100 and 500 meV for UPS and XPS, respectively. The light incident angle 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 500 Oe along the in-plane <1-10> 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 [16,17]. The base pressure during the experiment was $8\times10^{-11}$ mbars rising to $7\times10^{-10}$ mbars during metal evaporation. Thin YCo$_2$ films, with a thickness of 150 Å as measured by a quartz microbalance, were grown epitaxially on W(110) at RT by co-deposition of high-purity Y and Co metals (ratio for deposition rates was Y:Co = 1ML/min: 2ML/min) from carefully degased electron-beam evaporators. Subsequent
annealing at 300°C led to a well-ordered YCo₂(111) surface as indicated by LEED shown in Fig. 1. Quantitative analysis of photoelectron core-level spectra confirmed the expected stoichiometries of YCo₂ to within experimental accuracy and further showed minimal degrees of surface stoichiometry alteration (within ±5% for both species) or surface contamination (e.g., less than 0.1 monolayers of oxygen or carbon contaminant) during experiment.

The possibility to grow epitaxial YCo₂ films with (111) orientation on W(110) buffer layer was first demonstrated in work of Robaut et al. [18]. The above mentioned LEED image can be clearly understood from the following consideration of the crystallographic structure of the YCo₂(111)/W(110) system. The distorted hexagon in the right lower corner of Fig. 1 (lower part) is formed on the basis of unit cell of the W(110) surface (the unit vectors of this cell are marked by dark arrows). The bright arrows can be transformed to the unit vectors of the hexagonal cell of YCo₂(111) surface by slight distortion (mainly in <1-10> direction of the W(110) surface). The presented structure was also confirmed by LEED simulation performed by LEEDpat2 package [19].

Spin-resolved photoelectron spectroscopy study was performed with two different photon energies: \( h\nu = 21.2 \text{ eV} \) and 1253.6 eV, that allows to vary the escape depth of electrons from 7 Å to ~25 Å and respectively change from surface to bulk sensitive photoemission. In Fig. 2 the spin-resolved photoelectron spectra are shown in the upper part for \( h\nu = 21.2 \text{ eV} \) (right) and 1253.6 eV (left). As can be seen from this Figure, the spectra measured with high surface sensitivity (\( h\nu = 21.2 \text{ eV} \)) show the clear spin-asymmetry, while one those measured with high bulk sensitivity show weak (if any) spin-asymmetry. These results demonstrate for a first time the clear observation of surface magnetism on top of bulk paramagnetic material. Even at room temperature we observe a clear manifestation of the ferromagnetic ordering of the YCo₂(111) surface on top of paramagnetic bulk. This means that Curie temperature of the magnetically ordered YCo₂(111) surface is higher than room temperature.

Electronic and magnetic structure of YCo₂(111) surface were theoretically investigated in Refs. [15,20] within the framework of the local spin density approximation (LSDA) using a full potential linear augmented plane wave method. The surface was modeled using a slab geometry with Y- and Co-terminated YCo₂(111) surfaces. It was found that, almost independently on the termination and the size of the surface lattice relaxation, top Co surface layer is intrinsically magnetic and its magnetic moment quickly decays deeper into the bulk [15]. In Fig. 2 (lower panel) the theoretical results for Co-atom projected spin-resolved DOS and corresponding spin polarization for paramagnetic bulk YCo₂ (dashed area), Co- (thick line) and Y-terminated (thin line) for YCo₂(111) surfaces are presented. Experimental spin polarization (multiplied by 2 for better presentation) is also shown by solid circles. The spin polarization was calculated by the formula: \( P = (N^\uparrow - N^\downarrow) / (N^\uparrow + N^\downarrow) \), where \( N^\uparrow \) and \( N^\downarrow \) means number of spin-up and spin-down electrons in the valence band, respectively.
The formation of the surface magnetic moments in YCo$_2$ can be understood already within the itinerant picture of magnetism even on the basis of the calculated nonmagnetic DOS. In the DOS of paramagnetic bulk YCo$_2$ there is a peak in the close vicinity of $E_F$ (binding energy is less than 0.15 eV). For the surface Co layer of YCo$_2$(111), $E_F$ intersects at the top of the Co 3$d$ band with a DOS large enough to fulfill the Stoner criterion for the onset of magnetism. This increase of the surface DOS at $E_F$ is due to the reduced coordination number, which results in the well known band narrowing at the surface and subsequent shift of the 3$d$ states to maintain charge neutrality; for this almost filled 3$d$ band, the shift is toward higher energy. As it was shown [15,20] already by the third Co layer the DOS is largely bulk-like and the DOS is too small to fulfill the Stoner criterion.

Experimental and theoretical DOS are in good agreement as can be seen from Fig. 2: the spin-resolved structures in the vicinity of $E_F$ as well as in the binding energy range 1.5-2 eV are coincide. The calculated spin polarization (Fig. 2, right part of the lower panel) reproduces qualitatively the energy dependence of the measured polarization. Particularly good agreement is obtained for the points where the spin polarization changes its sign and peak positions. The discrepancy between values of experimental and theoretical spin polarization can be easily explained by the temperature at which experiments were performed (RT) whereas all calculations were carried for $T = 0$ K. From another side, the observed difference between experimental and calculated values of spin polarization can be explained by the following consideration. Indeed He I$\alpha$ spectra are more surface sensitive than Mg K$\alpha$ ones but signal does not come exclusively from the surface (in the same way, Mg K$\alpha$ spectra contain also a small contribution from the surface). Then, He I$\alpha$ spectra carry polarization information from the paramagnetic bulk and from the ferromagnetic surface and the measured value is a weighted average of these two contributions.

In this paper we report about the experimental confirmation of an intrinsic magnetic surface on an otherwise paramagnetic bulk material. Our spin-resolved photoelectron spectra unambiguously show Co-atoms in the (111) surface layers of the intermetallic compound YCo$_2$ possess a sizeable magnetic moment, 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.

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