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Element specific magnetization has been determined at the surface and in the bulk of $Co_2Cr_{0.6}Fe_{0.4}Al$ Heusler alloy films grown on α-Al_2O_3 and capped by Al, using x-ray magnetic circular dichroism both in transmission and total electron yield. The magnetic moments for Co and Fe are considerably reduced at the upper surface in comparison to their values in the bulk of the film. The large reduction at room temperature of 17% for thick films averaged along the electron escape depth implies an even larger reduction at the topmost layer which is crucial for spin-dependent transport. The surface magnetization decreases additionally with respect to the bulk value with decreasing film thickness below 20 nm. © *2006 American Institute of Physics*.
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Materials with high spin polarization are a precondition for the future development of spin electronic devices.[1] For most application devices the relevant property is the spin polarization at the surface of the material instead of its bulk properties. For tunneling magnetoresistance devices the topmost atomic layer at the interface exclusively determines the tunneling magnetoresistance (TMR) value. Therefore, the evaluation of magnetic properties at the surface is important for the search of materials with high spin polarization and consequently high TMR values at the interface.

Nearly total spin polarization at the surface has been found for half-metallic $La_{2/3}Sr_{1/3}MnO_3$ from tunneling experiments[2] at low temperatures. Recently, research focused on half-metallic materials with a Curie temperature $T_C > 300$ K that are more favorable for applications. Heusler alloys with high T_C have been investigated, that were predicted or measured half-metallic in the bulk, but showed a considerable decrease of polarization at interfaces (Co_2MnSi,[3,4] Co_2MnGe,[5] NiMnSb[6]). In the case of NiMnSb it was shown that the surface composition has a critical influence on the polarization.[6] Wang *et al.*[3] revealed a small spin polarization of 10% only, although the magnetization at the surface seems not to be decreased. Theoretical considerations reveal that the symmetry breaking at the interface may cause a lack of high spin polarization.[7,8]

We focus on films consisting of the Heusler alloy $Co_2Cr_{0.6}Fe_{0.4}Al$ that was predicted to be half-metallic[9] and showed a huge magnetoresistance effect in a pressed powder specimen,[10] however, subsequent experiments on TMR devices with $Co_2Cr_{0.6}Fe_{0.4}Al$ as one of the magnetic contacts failed to show the expected high TMR[11–13] or giant magnetoresistance (GMR).[14] Point contact measurements indicate values of spin polarization below $P=0.5$.[15,16] We will clarify the question whether the apparently decreased spin polarization at the surface of $Co_2Cr_{0.6}Fe_{0.4}Al$ films is related to a decreased magnetization at or near the interface.

Quantitative information on element specific spin and orbital magnetic moment can be gained using x-ray magnetic circular dichroism (XMCD) in the x-ray absorption spectroscopy (XAS).[17] We simultaneously measure the XMCD signal in transmission and by total electron yield (TEY). As TEY is surface sensitive while the transmission signal averages along the complete film normal we can infer a tendency for the depth dependence of the magnetization. It has been shown previously that the combination of transmission and TEY avoids common errors of the XMCD analysis, when relative changes are considered.[17] Common errors include finite polarization of x-ray light, unknown number of unoccupied *d* states, background subtraction for transition into *s* states, and errors due to separation of L_3 and L_2 transitions. In our case the transmission signal was measured via the x-ray luminiscence within the substrate, thus allowing the investigation of epitaxially grown films, in contrast to previous approaches using parylene foil substrates.[17]

We show that the magnetic moments calculated from the surface sensitive TEY are reduced by 17% averaged over the electron escape depth of about 25 Å with respect to the corresponding moments determined from the transmission signal. Since a homogeneous magnetization reduction at the surface is unlikely the reduction infers an even larger reduction for the topmost layer and may explain the observed low TMR values and spin polarization at the Fermi level of the films.

We prepared thin films of the Heusler compound $Co_2Cr_{0.6}Fe_{0.4}Al$ with a $L2_1$ structure on α-plane $(11\bar{2}0)$ Al_2O_3 by magnetron sputtering.[18] The (110) and $(1\bar{1}0)$ Bragg planes of the film are parallel to the $(11\bar{2}0)$ and (0001) Bragg planes of the substrate, respectively. The films used for the present study were deposited at 300 °C which is lower than the temperature for optimal epitaxial growth but results in smoother films. After the deposition the films were annealed for 1 h at 450 °C in order to increase the magnetization. The

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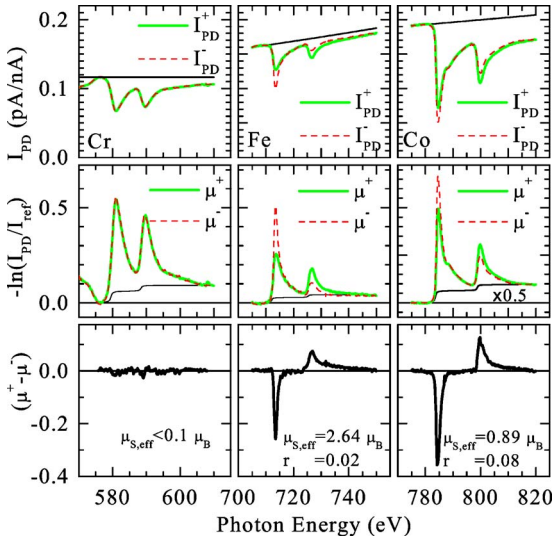

FIG. 1. (Color online) Absorption spectra obtained by transmission measurements at 300 K of a 110-nm-thick $Co_2Cr_{1-x}Fe_xAl$ Heusler alloy film grown on a-Al_2O_3 and capped by 6 nm Al. The top row shows the photodiode current normalized to the Au-net reference current and the assumed linear increasing reference signal I_{ref} of the sample. In the center row we plot the absorption μ and the step function. The bottom row shows the XMCD spectra.

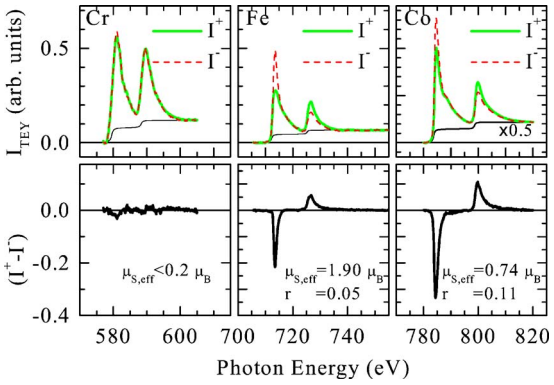

FIG. 2. (Color online) Absorption spectra obtained by TEY simultaneously measured as the data in Fig. 1.

films were capped *in situ* by 6 nm Al in order to prevent oxidation. The magnetization of the films measured by vibrating sample magnetometer (VSM) is $(3.4\pm0.3)\mu_B$ (300 K) and $(3.7\pm0.3)\mu_B$ (5 K) (values per formula unit).

The XAS experiments were performed at the UE56/1-SGM beamline at the German synchrotron light source BESSY II. The incident photon flux was monitored by a Au net. TEY was measured via the sample current. The sample was shielded by a conducting tube on a positive bias voltage (100 V) in order to collect all electrons. For the x-ray absorption in the transmission geometry the photon flux transmitted through the thin Heusler films was detected via x-ray luminiscence in the Al_2O_3 substrate.[19] The light intensity in the visible wavelength range escaping at the substrate edge was measured by a GaAs photodiode. Using a reference sample with an ultrathin Co layer on a 250-nm-thick Mo seed layer that is not penetrated by x rays we verified that no x-ray fluorescence light from the sample surface was detected by the photodiode. An external magnetic field of 1.6 T, that is sufficiently large to saturate the sample magnetization, was applied perpendicular to the film surface and flipped to determine the XMCD signal while the polarization was kept constant. XMCD was measured at 300 K and at 100 K.

Figure 1 shows the incident-photon-flux-normalized transmission XAS spectra of a 110-nm-thick Heusler alloy film taken with the magnetic field applied parallel (I^+_{PD}, solid curve) and antiparallel (I^-_{PD}, dashed curve) to the circular polarization of the incident photons. The reference spectra I_{ref} were assumed to increase linearly with the photon energy, normalized at the pre-edge region of the corresponding element (equivalent to an infinitely large penetration depth). This reference spectra is needed in order to calculate the relative absorption cross sections from the transmission spectra using the equation $\mu^{\pm}(h\nu)=-\ln[I_{\pm}(h\nu)/I_{ref}(h\nu)]/d$, where d is the thickness of the film.

The simultaneously measured TEY spectra normalized to the incident photon flux are shown in Fig. 2. After subtracting the background signal the XAS spectra were multiplied by a constant factor in order to achieve $(I^+_{TEY}+I^-_{TEY})=\mu^+ + \mu^-$ at the L_3 maximum. A quick inspection shows that the XMCD asymmetry in the TEY $(I^+_{TEY}-I^-_{TEY})$ (Fig. 2) is smaller than in the case of the transmission signal (Fig. 1). As observed for all three elements the step jump between pre- and postedge intensity is larger for the case of TEY compared to the transmission XAS, indicating a reduction of the number of d holes at the interface.

It is known that saturation effects in L-edge magnetic circular dichroism can considerably affect the sum-rule extraction of the number of d holes, spin moments, and orbital moments.[17] The degree to which saturation of the signal occurs in the electron yield signal depends on the relative photon penetration depth λ_x and electron escape depth λ_e. For a perpendicular incident photon beam the saturation effect can be expressed by an energy dependent correction factor $f=I_{TEY}/C\mu=1/(1+\lambda_e/\lambda_x)$. Values for λ_e scale in general with the mean number of d holes that was calculated for the present compound as $\bar{n}_d=2.4$. Therefore, one may assume, that the electron escape depth can be approximated by the value of Co, $\lambda_e=25$ Å,[17] for all three elements Co, Fe, and Cr. This value also determines the information depth of TEY. The x-ray penetration length λ_x is the inverse of the x-ray absorption coefficient μ as obtained from the transmission signal. The penetration length in the pre-edge region was assumed to be infinitely large, which gives only a minor error. For Co, Fe and Cr we thus obtain the minimum values at the L_3 edge $\lambda_{x,min}(Co)=960$ Å, $\lambda_{x,min}(Fe)=2880$ Å and $\lambda_{x,min}(Cr)=1920$ Å. These values are considerably larger than values for pure element films ($\approx$200 Å). This observation can be explained by the effective dilution of the corresponding element in the Heusler alloy and by the attenuation of the total number of electrons in the compound due to the Al content. The maximum deviation of the correction factor from unity at the L_3 edge of Co is $1-f=0.026$ and even less for the other two elements. The saturation effect thus leads to a reduction of the spin moment as determined from TEY of about 3% and we conclude that the saturation effect correction can be neglected in our case.

Magnetic moments have been determined as a function of the thickness of the films as shown in Fig. 3 applying the sum-rule analysis with numbers of d holes $n_d(Cr)=6$, $n_d(Fe)=3.4$, $n_d(Co)=2.5$ according to numerical

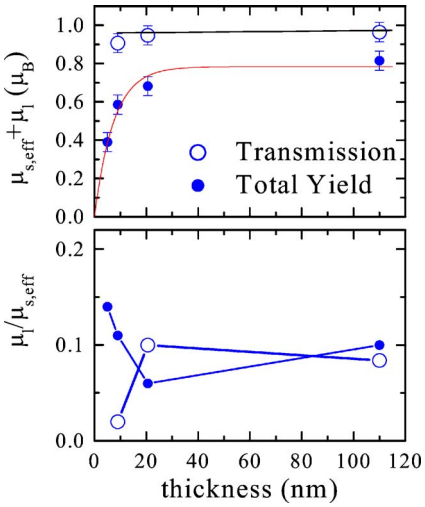

FIG. 3. (Color online) Magnetic spin moment and orbital to spin ratio for Co in $Co_2Cr_{1-x}Fe_xAl$ Heusler alloy films from transmission and TEY as a function of film thickness measured at 300 K. The absorption in the thinnest film was too small to perform the sum-rule analysis.

calculations.[20] The variation of the number of unoccupied *d* states might also be estimated from the ratio of the total absorption intensity as determined by integration of the helicity-averaged spectrum after subtraction of a step-like background and the step height of this background. A comparison of TEY and transmission signals indicates a decrease of unoccupied *d* states at the surface by $(10\pm5)\%$, which would further reduce the sum-rule values of magnetic moments. In order to keep the analysis straightforward we use identical parameters and integration boundaries for the sum-rule analysis of transmission and TEY signals including the number of *d* holes.

Below a thickness of 20 nm the near-surface magnetic moments start to decrease significantly, while the bulk values are less reduced. This observation cannot be attributed to a "normal" magnetic size effect at finite temperature which reduces moments only in the topmost 1–2 atomic layers. The comparatively weak thickness dependence of the transmission signal is in agreement with the film magnetization being independent of the film thickness as determined by VSM magnetometry. The orbital magnetic moments determined from TEY show a tendency to increase at low thicknesses as observed also for Co_2MnSi films.[3]

The TEY averages the magnetization $m(z)$ along the depth z according to $\bar{m}=(1/\lambda_e)\int m(z)\exp(-z/\lambda_e)dz$. Assuming that the magnetization exponentially approximates the bulk value m_0 according to $m(z)/m_0=1-r\exp(-z/\lambda_m)$, one calculates a relative magnetization reduction r at the surface (relevant, e.g., for TMR devices) of $r=(1-\bar{m}/m_0)\times(1+\lambda_e/\lambda_m)$. Using the value $1-\bar{m}/m_0=0.17$ determined for thick films, r can be determined if one knows the magnetic correlation depth λ_m. From the data $1-\bar{m}/m_0=0.33$ of the 10 nm film and the precondition that $r\leqslant 1$ we find the relation $\lambda_m\geqslant 1.25$ nm. On the other hand, the fact that the bulk moment of the 5 nm film does not appear significantly reduced indicates that λ_m should be at most half that value, i.e., $\lambda_m\leqslant 2.5$ nm. We conclude that for thick films the relative magnetization reduction at the topmost surface is $r=0.25-0.51$.

The observed reduction can only partly be attributed to a temperature dependence: Low-temperature experiments (100 K) indicate an increase of the Co XMCD signal by 8% compared to the value obtained at 300 K. No oxidation is found at the interface. The most probable explanation is therefore a disturbed atomic structure, e.g., Cr atoms occupying Co positions not only at the topmost layer but within an extended interface region. Moreover, it cannot be excluded that an interdiffusion of the Al capping layer with the Heusler alloy took place. This interpretation is supported by the observation of a decrease of the number of *d* holes at the interface.

In summary, the magnetic moments of Fe and Co in $Co_2Cr_{0.6}Fe_{0.4}Al$ thick (100 nm) films calculated from the surface sensitive TEY are reduced by 17% averaged over the electron escape depth of about 25 Å with respect to the corresponding moments determined from the transmission signal. The near-surface magnetization decreases with decreasing film thickness, while the bulk magnetization of the film remains unaffected. Our finding of a significant magnetization reduction at the surface of the Heusler alloy of 25%–51% may explain the previously found unexpected low TMR/GMR and spin polarization values.

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