Negative dependence of surface magnetocrystalline anisotropy energy on film thickness in $Co_{33}Fe_{67}$ alloy*

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(Received 1 April 2016; revised manuscript received 31 May 2016; published online 25 August 2016)

In this work, the magnetocrystalline anisotropy energy (MAE) on the surface of $Fe_{33}Co_{67}$ alloy film is extracted from x-ray magnetic linear dichroism (XMLD) experiments. The result indicates that the surface MAE value is negatively correlated with thickness. Through spectrum calculations and analysis, we find that besides the thickness effect, another principal possible cause may be the shape anisotropy resulting from the presence of interface roughness. These two factors lead to different electron structures on the fermi surface with different exchange fields, which produces different spin–orbit interaction anisotropies.

Keywords: magnetocrystalline anisotropy energy, x-ray magnetic linear dichroism, $L_{2,3}$ edge, ligand field multiplet

PACS: 75.30.Gw, 75.70.Rf, 75.50.Bb **DOI:** 10.1088/1674-1056/25/10/107501

1. Introduction

The enormous increase in the recording density of a hard disk has mainly been achieved by scaling the dimensions of the bits recorded in the storage layer. The capacity of the data recording density is characterized by the magnetocrystalline anisotropy energy (MAE). Hence, controlling or manipulating the magnetocrystalline anisotropies in thin films and multilayers[1,2] is attractive technologically. Moreover, the MAE is fundamentally interesting, because of the interplay among charge, spin and lattice structure in the interface and surface. Several decades ago, Bruno[3] first proposed that the MAE is proportional to the expectation value of the orbit moment. Although the proposition was later corroborated by Weller *et al.*,[4] the model is not suitable for all situations. In 1999, Gerrit van der Laan derived that the MAE is directly related to the anisotropic part of the spin–orbit interaction, rather than to the orbital part of the magnetic moment. Meanwhile, he also demonstrated that the sum and weighted difference signals over the L_2 and L_3 edges in the x-ray magnetic linear dichroism (XMLD) spectrum are proportional to the anisotropy in the charge distribution and spin–orbit interaction, respectively.[5] The anisotropy spin–orbit interaction, which can be extracted from data measured by XMLD, is related to the MAE. Therefore the XMLD can be used as a valuable tool to measure the MAE of thin films and multiplayers.[6,7] Fe_xCo_{1-x} alloy is one of Heusler alloy compounds which were extensively studied. The orbital moment and MAE of Co have maxima when x is around 0.6, i.e., $x \sim 0.6$.[8–10] Some reports showed that the MAE of Fe–Co alloy is about 100 μeV/atom–200 μeV/atom,[11] or even up to 700 μeV/atom–800 μeV/atom.[12] In the present work, we report the effect of the sample thickness on the surface MAE of $Co_{33}Fe_{67}$ films using the XMLD method.

2. Experiment

Alloy films with different thickness (5, 20, 50, 71, and 95 nm) were prepared on Si (100) substrates by DC magnetron sputtering at room temperature. Single composite targets containing 67% Fe and 33% Co were used. The base pressure of the chamber was below 1×10^{-3} Pa, and the sputtering pressure of argon was 0.13 Pa. The film depositing rate was controlled to be about 1 Å/s. After deposition, films were capped with 3.5 nm Ta to prevent it from oxidizing. XMLD experiments were carried out at 3W1B[11] beamline of Beijing Synchrotron Radiation Facility (BSRF). The degree of linear polarization of the beam used was about 92%. A planar grating monochromator was used to generate soft x-ray in an energy range of 50 eV–1500 eV which covers $L_{2,3}$ edges of 3d transmission metals. The saturation magnetization field was typically about 300 Oe (1 Oe = 79.5775 A·m^{-1}) for those alloy films. And thus the external field provided by a pair of permanent magnets was about 4000 Oe that enabled those samples to be magnetized to the saturated states. During the measurements, the polarization plane of incident light and the sample are fixed. At each energy point, the direction of magnetization was continuously rotated so as to be parallel or perpendicular to the polarization plane of incident light. The x-ray absorption spectra (XAS) and XMLD spectra of alloy films recorded

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11075176 and 11375131).

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in total electron yield (TEY) mode. The results for Co and Fe are shown in Figs. 1 and 2, respectively.

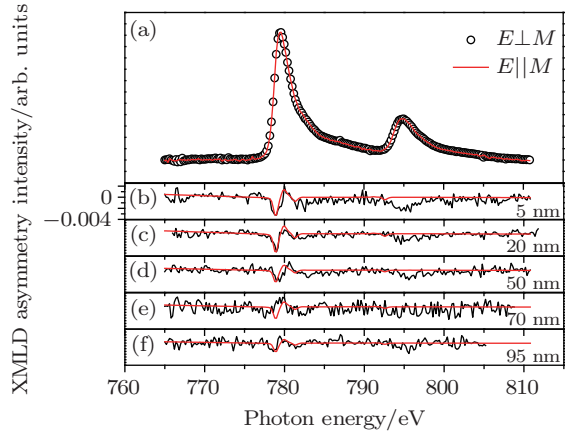


Fig. 1. (color online) (a) Co $L_{2,3}$ x-ray absorption spectra for the 5-nm film when the direction of magnetization is parallel (red line) and perpendicular (black line) to the polarization plane of incident light. (b)–(f) Co edge XMLD spectra (black line) and the corresponding calculated results (red line) of alloy films in a thickness range from 5 nm to 95 nm.

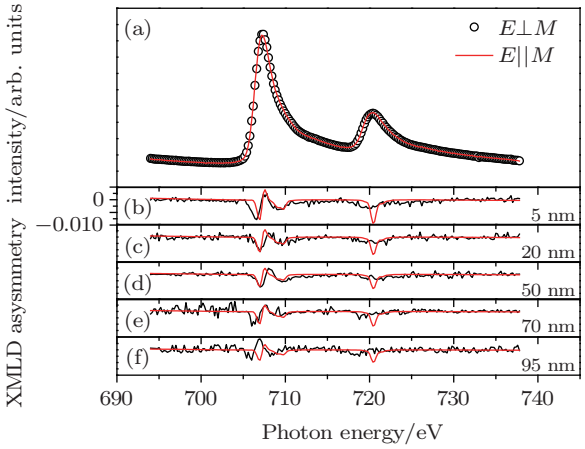


Fig. 2. (color online) (a) Fe $L_{2,3}$ x-ray absorption spectra for the 5-nm film when the direction of magnetization is parallel (red line) and perpendicular (black line) to the polarization plane of incident light. (b)–(f) Fe edge XMLD spectra (black line) and the corresponding calculated results (red line) of alloy films in a thickness range from 5 nm to 95 nm.

3. Results and discussion

The MAEs can be extracted from the XMLD and XAS spectra using the following procedure. All XAS are normalized at L_3 peak. The background is subtracted from the XAS in order to isolate the contributions of the 2p→3d transitions for Co and Fe absorption spectra. In the present study, we use a two-step-like function background to account for non-resonant absorption as reported in Ref. [13]. Some integral quantities coming from sum rules are needed. $\Delta I_{L_3}+\Delta I_{L_2}$ denotes the integrated XMLD signal. $I_{||}+I_{\perp}=(I_{L_{3||}}+I_{L_{2||}})+(I_{L_{3\perp}}+I_{L_{2\perp}})$ is the integrated XAS signal of L edges.[5,6] These integrals can be calculated by integrating over the L_3 or L_2 edge of XAS and XMLD spectra obtained under corresponding parallel (||) or perpendicular (⊥) experimental condition. The ratios $(\Delta I_{L_3}+\Delta I_{L_2})/(I_{||}+I_{\perp})$ of Co and Fe in different samples are listed in Table 1. The integrated XMLD signals account for about 0.01%∼0.04%, indicating that there is no change in the charge anisotropy when the magnetic field direction changes.

Table 1. Ratios $(\Delta I_{L_3}+\Delta I_{L_2})/(I_{||}+I_{\perp})$ for Co and Fe in $Co_{33}Fe_{67}$ alloy films with different thickness.

Ratio	Element	5 nm	20 nm	50 nm	71 nm	95 nm
$(\Delta I_{L_3}+\Delta I_{L_2})/(I_{||}+I_{\perp})$	Fe	0.01%	0.03%	0.02%	0.04%	0.02%
	Co	0.04%	0.02%	0.03%	0.02%	0.01%

According to the XMLD sum rules, we use the following equations to calculate MAE (ΔE):[5,6,14,15]

$$\frac{\delta_{M_\perp}-\delta_{M_{||}}}{\rho}=\frac{\delta'}{\rho}=\frac{8}{5}\sqrt{3}\frac{\langle\lambda_a\rangle}{n_h}, \tag{1}$$

$$\Delta E=\frac{1}{2}\varsigma\langle l\cdot s\rangle=\frac{\varsigma}{2}\langle\lambda_a\rangle. \tag{2}$$

With $\varsigma=50$ meV,[3,6] $n_h=2.49$ for Co and $n_h=3.39$ for Fe,[16] MAE values of Co and Fe can be calculated, respectively. The MAE values of Co and Fe for different films are shown in Fig. 3. It shows that both Co and Fe have the same change tendency. The MAE increases with the decrease of film thickness. The maximum MAE values are 516 μeV/atom for Fe and 606 μeV/atom for Co of 5-nm-thick film, respectively. The minimum MAE values are 279 μeV/atom for Fe and 360 μeV/atom for Co of 95-nm-thick film, respectively. According to Ref. [6], the MAE measured with XMLD is 30–40 times that with surface magneto-optical Kerr effect (SMOKE). MAE values corrected are of the order of a few tens μeV/atom that is in accordance with the previous result.[9,17]

Because the probing depths of total electron yield of soft x-ray absorption experiments of Fe and Co metals are both about 40 Å.[18] These MAE values reflect the surface magnetisms of samples. To identify the physical mechanisms, we need to resort to quantitative explanations of the XMLD spectra. We perform a simulation of the XMLD spectra of Co and Fe using the ligand field multiplet (LFM) model and compared with the spectra.[13,19–21] LFM calculations as shown in Fig. 1 are performed by using the CTM4XAS 5.2 program, including spin–orbit couplings, crystal field effects, exchange fields and reductions of the Slater integrals $F(dd)$, $F(pd)$, and $G(pd)$ to include the interatomic configuration interaction.[22,23] The simulations cover the L_3 edge, and some differences appear in L_2 edge, especially for Co, since the 3d bands are delocalized. When the film is thicker, the difference is more obvious. That is because the experiment XMLD signal is small. The following parameters are obtained by comparing the calculated spectra with the experimental spectra: 2p and 3d spin–orbit interactions, which are reduced by being multiplied by factors of 0.82 and 0.80, respectively, for the cobalt cations, while factors of 1.0 and 0.8 are used for iron cations. The Slater integrals $F(dd)$, $F(pd)$, and $G(pd)$ are taken to be 40%, 60%, and 80% of the Hartree–Fock values, respectively, for the cobalt cations, and 40%, 100%, and 80%, respectively, for the iron

cations. The crystal field splittings of samples with different thickness are slightly different, which are just 0.02 eV–0.03 eV between the 5-nm-thick film and 95-nm-thick film for Co and Fe. The most obvious difference is the exchange field parameter. In particular, for both Co and Fe, the exchange field values are both about 0.1 eV for 5-nm-thick film and about 0.03 eV for 95-nm-thick film, respectively. From the simulation, it shows that the crystal field splitting plays a trivial role and the exchange field plays an important role in the shape and magnitude of L_3 edge of XMLD spectra. Furthermore, as shown in Fig. 3, the variations of both MAE value and exchange field parameter with thickness are similar, which suggests that they have some close relations.

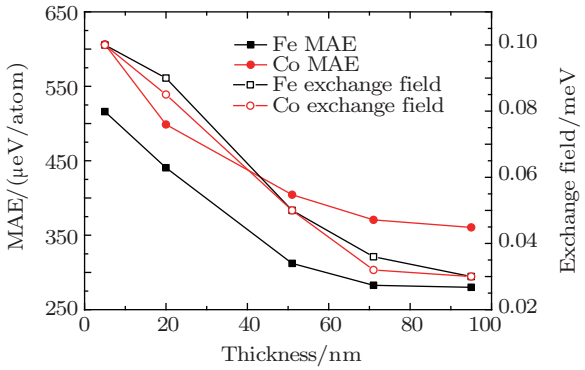


Fig. 3. (color online) Variations of MAE value and exchange field with thickness for Fe (black diamond dot) and Co (red circle dot) of $Fe_{33}Co_{67}$ alloy films. Black empty diamond dots and red empty circles denote the exchange field values of Fe and Co respectively. Lines are guides for eyes.

The exchange field related to the interatomic exchange interaction in 3d metal can be treated as a magnetic field acting only on spin S. It is included by a term $g\mu_B HS$ in the Hamiltonian. This field lifts the degeneracy, making the energy of the M_J sublevels equal to $-g\mu_B HM_J$. When exchange interaction is of the same order of magnitude as the spin–orbit interaction ($\zeta = 50$ meV), the different J levels are strongly mixed.[14] Form the XMLD spectrum calculation parameters, the value of the exchange field is 0.1 eV for 5 nm which is larger than that of 0.03 eV for 95 nm. It suggests that the thinner film gives an enhancement of the spin moment. The exchange field versus thickness and MAE versus the thickness have the same variation tendencies, which reveals the reason why different electron exchange fields leading to different MAE values may relate to the electron structure. Kuneš *et al.*[24] and Oppeneer *et al.*[25] derived that the XMLD spectrum is proportional to the energy derivative of the exchange polarization of the unoccupied 3d-density of states. Hence, the different magnitudes of XMLD in L_3 edge measured in the present work lead to the redistribution of 3d states in the vicinity of Fermi energy.

In addition, magnetocrystalline anisotropy is expected to change as the symmetry of atoms changes. Usually, the effective anisotropy constant K is used to describe anisotropy. The MAE is proportional to the K. The K is expressed as[26]

$$K = \frac{2K_{\text{surface}}}{d} + K_{\text{voulume}} - \mu_0 M^2. \tag{3}$$

The first term on the right-hand side in Eq. (3) is the ratio between the anisotropy contribution from the surface of the film and that from film thickness, d. The second term is the volume anisotropy brought about by lattice mismatching. The last term denotes the shape anisotropy, which is related to the interface roughness. Figure 4 shows that there are the discrepancies between the first term of K and the MAE values of Fe and Co after normalization. For the normalized K first term curve, it needs either to raise the latter section or to debase the first section. It is necessary to consider the last two terms. The second term, K_{voulume}, can be attributed to the volume anisotropy, which refers to the effect of lattice mismatching. However, the calculation indicates that the crystal field splitting changes slightly with thickness. Then we come to discuss the third term, $-\mu_0 M^2$, which reminds us of the exchange field parameter. They are proportional to moment square and moment respectively and have the same variation tendencies, which can make the K curve tend to the experimental MAE curve and account for the discrepancy qualitatively. It infers the reasons why the MAEs of films are different for different thickness, besides the thickness effect, another principal possible cause is related to the shape anisotropy coming from the interface roughness. These two factors lead to the change in the density of 3d states near the Fermi surface with different exchange fields, resulting in different spin–orbit interaction anisotropies, namely, different MAE values.

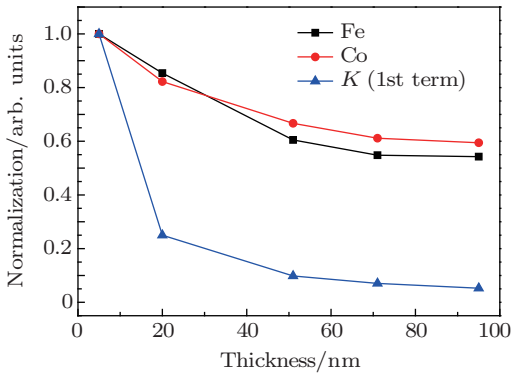


Fig. 4. (color online) Comparisons among the plots of normalization values of Fe MAE (black diamond dot), Co MAE (red circle dot), and the first term of K (blue triangle dot) versus thickness. Lines are guides for eyes.

4. Conclusions

In this work, we find that the XMLD sum rule is applicable due to the large sensitivity of spin–orbit anisotropy to MAE and we use the XMLD to calculate the element-specific MAE values on surfaces of $Co_{33}Fe_{67}$ alloy films with different thicknesses. From the XAS and XMLD spectra and sum rules, the integrated XMLD signal is nearly zero. It is evident

that the anisotropy arises from the magnetism while there is no contribution from the charge anisotropy. From the MAE calculations, firstly, we find that the MAE values decrease with the increase of the film thickness for both Co and Fe elements. Secondly, the differences in L_3 edge of XMLD indicate the redistribution of 3d states near Fermi level. The most important result is that the variation tendency of exchange field parameter with sample thickness is the same as that of MAE versus sample thickness. It implies that there is a close relationship between them. By comparing with the anisotropy constant K, the reason for different MAE values may result from two causes. Besides thickness effect, the shape anisotropy relating to the interface roughness plays an important role in the thickness dependence on the surface MAE of film. These two factors cause redistribution of 3d electron states to change the absorption atom local circumvent and bring about the variable field felt by itself, which produces different spin–orbit interaction anisotropies, viz. different MAE values.

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