Magnetic moment investigations of epitaxial magnetite thin films

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In this report, we provide an x-ray magnetic circular dichroism (XMCD) study for 100 nm thick epitaxial magnetite (Fe_3O_4) films on MgO (001) and Al_2O_3 (0001) substrates. For XMCD, we recorded the surface sensitive total electron yield and the bulk sensitive transmission spectra. From the analysis of the XMCD data, we find an increased Fe spin moment (10% larger) at the surface of the film on MgO (100) with respect to the corresponding bulk value of the film. Surface and bulk spin moments of the film on Al_2O_3(0001) are almost equal. For both films, the bulk orbital to spin moments ratio increases from zero at 70 K to 0.03–0.04 at 300 K. For Fe_3O_4/MgO (001), the surface orbital to spin moment ratio behaves similarly to the bulk value, while the orbital to spin moments ratio is increased at the Fe_3O_4/Al_2O_3 (0001) surface to 0.06. The observed differences between films grown on MgO and Al_2O_3 are explained within the framework of differences in mismatch strain experienced by the films. © *2008 American Institute of Physics.*
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INTRODUCTION

Magnetite (Fe_3O_4) is one of the promising materials for spin electronic applications due to its half-metallic nature, high Curie temperature, and a first order charge ordering transition at around 120 K (Verwey transition).[1,2] These properties generated a renewed interest in studying the physical properties of epitaxial structures based on magnetite. Consequently, there are several reports on magnetic and transport property investigations on epitaxial films grown on a variety of substrates using various deposition methods.[3–6] Differences in crystal symmetry and extent of lattice mismatch strain between Fe_3O_4 and substrate material are expected to influence the magnetic properties and even the band structure. The band structure of high temperature conducting phase of Fe_3O_4 is predicted to be half-metallic on the basis of first principles calculations based on the local density approximation (LDA), in which minority spin electrons are responsible for conduction.[7,8] These band structure calculations give a magnetic moment of $4\mu_B$/f.u. for magnetite. However, some recent experimental results suggest that the itinerant electron picture for Fe_3O_4 is more adequate than the localized electron model.[9,10] Despite rigorous efforts during the past decade, complete understanding of the nature of 3d electronic correlations and complex band structure of magnetite are still a key issue.

High energy spectroscopies such as x-ray magnetic circular dichroism (XMCD) provide valuable information on the band structure of magnetic materials, as well as the site specific spin and orbital moments.[11] The XMCD has been employed to investigate the spin structure of magnetite. In a recent investigation, Huang *et al.*[12] reported a large unquenched *B*-site orbital moment of $0.33\mu_B$, which has been attributed to a strong on-site Coulomb interaction and corresponding 3d electron correlation effects. They obtained within the LDA+U scheme similar values of unquenched orbital moments. However, further band structure calculation report only a small value of orbital moments.[7,8] Contrary to the observation of Huang *et al.*, Goering *et al.*[13] reported nearly vanishing orbital moments for a Fe_3O_4 bulk crystal. We employ XMCD to investigate the nature of 3d electrons in single crystalline Fe_3O_4 films. In this paper, we report the results on XMCD measurements performed in the soft x-ray absorption for epitaxial magnetite films on MgO (001) and Al_2O_3 (0001) substrates grown under identical conditions. Due to a small lattice mismatch, the films grown on MgO are fully strained, whereas the one grown on Al_2O_3 is fully strain relaxed owing to a larger lattice mismatch (7.8%).

EXPERIMENTAL

Epitaxial Fe_3O_4 thin films of 100 nm thickness used in the present study were grown on MgO (001) and Al_2O_3 (0001) substrates under identical conditions using oxygen plasma assisted molecular beam epitaxy system (DCA MBE M600). The base pressure of the system is 5×10^{-10} Torr. The growth of the films was carried out at a substrate temperature of 250 °C. The details of the growth process are given elsewhere.[14] Reflection high-energy electron diffraction (RHEED) was used to determine the growth mode and growth rate. The epitaxial relationship of both the heterostructures was established from the knowledge of in-plane ($a_\parallel$) and out-of-plane ($a_\perp$) lattice parameters determined from ω-2θ rocking curves measured using a multicrystal high resolution x-ray diffractometer. Magnetization measure-

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ments were performed using a vibrating sample magnetometer (VSM) (PPMS-14T, Quantum Design, USA).

X-ray absorption spectroscopy (XAS) was measured at the UE56/1-SGM beamline at the synchrotron light source BESSY II (Berlin) with perpendicularly incident photons and an external magnetic field of 1.0 T applied parallel to the photon beam. The x-ray luminescence in the substrate[15] measures the photon flux transmitted through the film [transmission (TM) signal]. This information reflects the film properties integrated along the film normal. The simultaneously measured total electron yield (TEY) via the sample current serves as surface sensitive information with a probing depth of 0.8 nm for Fe_3O_4.[13] For XMCD, we take the difference of spectra recorded with opposite magnetization direction.

RESULTS AND DISCUSSIONS

Prior to discussing the results of magnetic circular dichroism on these films, we would like to point out that the films are highly stoichiometric, as determined from *in situ* RHEED and *ex situ* high resolution x-ray diffraction measurements. From the analysis of symmetric (200/400) and asymmetric (311/622) Bragg diffraction for the Fe_3O_4/MgO(001) heteroepitaxial system, we find that the films are fully strained.[14] The values of *in-plane* and out-of-plane lattice parameters for Fe_3O_4 film on MgO being 0.8426 and 0.8372 nm, respectively. Similar investigations for films on Al_2O_3 (0001) substrates suggest that the film was almost completely strain relaxed (out-of-plane lattice parameter for film is 0.8378 nm) in the sense that most of the epitaxial lattice mismatch strain has relaxed. This is due to the greater lattice mismatch of Fe_3O_4 with Al_2O_3 (7.8%, compressive) as compared to MgO (0.33%, tensile). Yet, it should be noticed that even 90% strain-relaxed film Fe_3O_4/Al_2O_3 has still more strain than completely unrelaxed Fe_3O_3/MgO film. In addition to the structural characterization, the presence of the Verwey transition in our samples was used as a further affirmation to the fact that the films are highly stoichiometric, as this transition is very sensitive to the deviation from the stoichiometry. Figure 1 shows the magnetization for both the samples as a function of temperature measured in the presence of 200 Oe field. The structural change at the Verwey transition invokes changes of the magnetization state presumably caused by a decreased magnetic anisotropy. The increase of the observed moment sensitively detects the change of the magnetization state at the transition temperature. It is clear that both films exhibit the Verwey transition. The Verwey transition temperature (T_V) is 123 K for the film on Al_2O_3, whereas its value is 119 K for the film on MgO.

We show a typical XAS and XMCD spectrum in Fig. 2(a). The general shape of the XAS spectra is comparable to the results presented for bulk Fe_3O_4.[12,13] The discussion of minor differences between the TEY and TM XAS spectra and between spectra measured below and above T_V exceeds the scope of this article. The integrated XMCD signal [Fig. 2(b)] exhibits a nonvanishing slope between 730 and 765 eV. The nonvanishing slope indicates a small and reproducible XMCD signal above the L_2 edge region, similar to the one observed in Ref. 13.
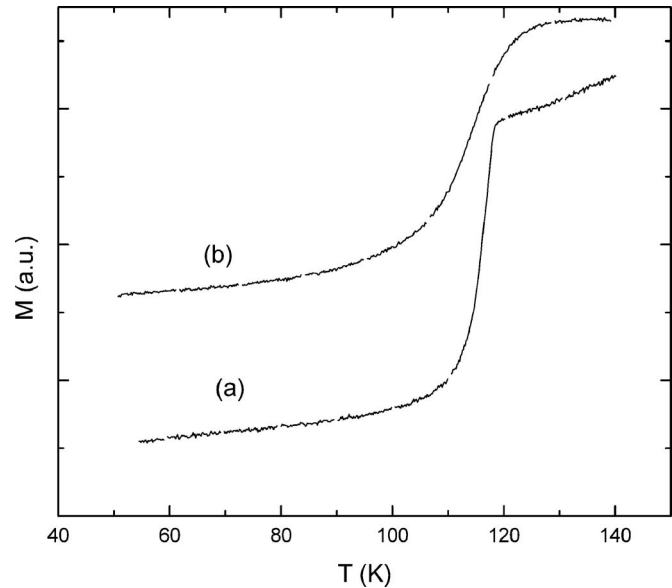

FIG. 1. Magnetization as a function of temperature for the 100 nm Fe_3O_4 films on (a) MgO (001) and (b) Al_2O_3 (0001) substrates. The magnetization was measured in a 200 Oe field during the warming cycle after cooling the sample from room temperature to 50 K in zero field.

We have applied sum rules for the L_2 edge integration range of 718–770 eV. The two-step background signal μ_{bg} that has been subtracted is shown in Fig. 2(a). For the number of Fe 3*d* holes, we assumed a value of N_h/Fe=13.5/3, identical to the value used in Ref. 13. Consideration of self-absorption effects is not applicable for TM XAS and can be neglected in the case of TEY XAS.[13] Results are shown in Table I. For the orbital to spin moment ratio μ_{spin}/μ_{orb}, the estimated error bar reflects data noise and uncertainties due to the integration range. For the effective spin moment $\mu_{spin}=(\mu_s+7\langle T_z\rangle)$, an additional error arising from the uncertainty of the background subtraction must be considered. Ad-
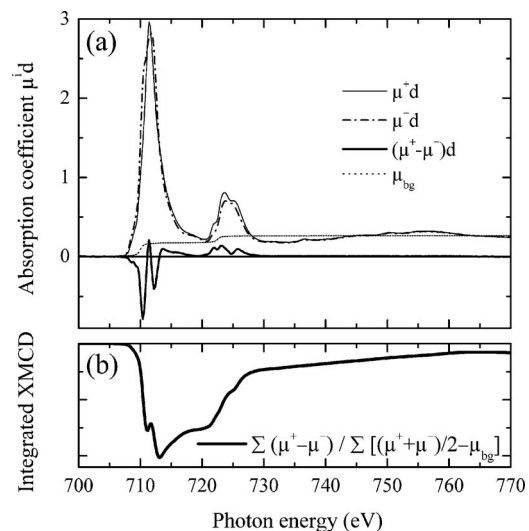

FIG. 2. (a) X-ray absorption coefficients μ^i for magnetization parallel and antiparallel to the x-ray polarization vector multiplied by the film thickness *d* and XMCD spectrum $\mu^+-\mu^-$ of a 100 nm Fe_3O_4 film on Al_2O_3 (0001) at 300 K (normal-incidence transmission geometry). (b) Integrated XMCD spectrum used for sum rule analysis.

TABLE I. Effective magnetic spin moment per Fe atom and orbital to spin moment ratio as determined by the sum rules from the XMCD spectra. Total Fe moment recalculated from the saturation magnetization as determined by VSM for the same samples are given for comparison. Values in parenthesis indicate the error bar.

	77 K $\mu_{spin}(\mu_B)$	77 K μ_{orb}/μ_{spin}	300 K $\mu_{spin}(\mu_B)$	300 K μ_{orb}/μ_{spin}	300 K $\mu_{VSM}(\mu_B)$
Fe_3O_4/MgO					
TM	0.86(2)	0.01(1)	0.74(13)	0.03(3)	1.36
TEY	0.99(2)	0.00(2)	0.99(2)	0.04(2)	
Fe_3O_4/Al_2O_3					
TM	0.89(2)	0.01(1)	0.91(2)	0.025(10)	1.2
TEY	0.86(2)	0.06(2)	0.87(2)	0.04(2)	

ditional systematic errors (same factor for all values given in Table I) due to the finite x-ray polarization and to the unknown exact value of N_h were neglected.

Only a minor temperature dependency of the spin moment is observed, in agreement with the saturation magnetization data from VSM measurements and comparable with data from a bulk Fe_3O_4 crystal.[13] The saturation magnetization of the films (see Table I) is in agreement with the bulk value for Fe_3O_4. However, μ_{spin} measured by XMCD is for both films about 30% smaller than the saturation magnetization measured for these samples by VSM magnetometry. We attribute this discrepancy to the error in determining the moment from VSM measurements and partly to the finite x-ray polarization.

A remarkable result is the increase of the surface spin moment of Fe_3O_4/MgO with respect to the bulk value of the film. This fact might be attributed to the smaller average coordination number for atoms at the surface. An increased surface moment was not observed in the case of Fe_3O_4/Al_2O_3, indicating a counteracting influence of antiphase boundaries.

It is also remarkable that the difference between surface and bulk moments is comparatively small despite the fact that the samples have been stored in air for several days. This observation indicates that the surface of the Fe_3O_4 films does not react considerably with oxygen at ambient conditions, thus implying a promising precondition for industrial processing.

The average orbital moments are much smaller than those reported in Ref. 12. At 77 K, the bulk values of both films are only $0.01\mu_B$, confirming the vanishing orbital moment contribution found for a bulk Fe_3O_4 crystal.[13] At 300 K, the orbital moment has increased to $0.03\mu_B$. This might be attributed to the thermally induced epitaxial strain. An increase of the orbital moment at the surface is not significant except the low-temperature TEY value of the

Fe_3O_4/Al_2O_3 (0001) film. In general, a larger surface orbital moment could be expected because of decreased crystal symmetry at the surface.

In summary, we determined element-specific magnetic spin and orbital moments at the surface and in the bulk of epitaxial Fe_3O_4 films in two orientations. Magnetization measurements at low field clearly confirm the presence of a Verwey transition in the films. The saturation magnetization is close to reference values found for a bulk Fe_3O_4 crystal, thus confirming the good quality of the investigated films. At 77 K, we found an increased surface spin moment for Fe_3O_4/MgO (001) and an increased surface orbital moment for Fe_3O_4/Al_2O_3 (0001).

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