

Unconventional Magnetization of Fe₃O₄ Thin Film Grown on Amorphous SiO₂

Substrate

Zhi-Guo Liu, Shang-Fei Wu, Jia-Xin Yin*, Wen-Hong Wang, Wan-Dong Kong, Hao-Jun Yang, Pierre Richard, Hong Ding, Lei Yan*

Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Collaborative Innovation Center of Quantum Matter, Beijing 100190, China

*E-mail: jiaxinyin@iphy.ac.cn; lyan@iphy.ac.cn.

High quality single crystal Fe₃O₄ thin films with (111) orientation had been prepared on amorphous SiO₂ substrate by pulsed laser deposition. The magnetization properties of the films are found to be highly unconventional. The Verwey transition temperature derived from the magnetization jump is around 140K, which is higher than the bulk value and it can be slightly suppressed by out-plane magnetic field; the out-of-plane magnetization, which is unexpectedly higher than the in-plane value, is also significantly increased as compared with the bulk value. Our findings suggest that the local Coulomb correlation U and the effective ferromagnetic exchange interaction J of Fe 3d electrons are both dramatically strengthened and out-of-plane directionally entangled by the unusual coupling between Fe₃O₄ thin film and the amorphous SiO₂ substrate.

Magnetite (Fe_3O_4) is one of the well-known ferrimagnetic materials, which has been attracting a lot of attention due to its unique electrical and magnetic properties, such as low electrical resistivity at room temperature, high Curie temperature (858 K), 100% spin polarization [1-4]. These properties make Fe_3O_4 a promising candidate for spintronic devices [5,6].

Magnetite has a cubic inverse spinel structure that is based on a face-centered cubic (fcc) lattice of oxygen anions. The cubic unit cell of Fe_3O_4 contains 32 oxygen anions and 24 iron cations, *i.e.* 8 Fe^{2+} and 16 Fe^{3+} ions which occupy interstices of oxygen ions; 8 tetrahedral (A) sites solely occupied by Fe^{3+} ions whereas 16 octahedral (B) sites equally shared by Fe^{3+} and Fe^{2+} ions. The magnetization of magnetite can be viewed as that the magnetic moments within the A and the B sublattices are ferromagnetically aligned while the two sublattices are antiferromagnetic with respect to each other.

At the room temperature, electrons continuously rapidly hop between Fe^{2+} and Fe^{3+} cations at B sites, leading to a fairly low electrical resistivity. Upon cooling, bulk Fe_3O_4 undergoes a metal–insulator transition termed as the Verwey transition [1,4]. Below 120 K, the hopping action is frozen and consequently the resistivity is increased by two orders of magnitude with a concomitant decrease in the magnetic moment. This transition is generally from a disordered phase to a charge ordered phase of Fe^{2+} and Fe^{3+} cations [7-11].

Epitaxial Fe_3O_4 thin films have some physical properties that differ significantly from those of bulk single crystals, such as distinct transition temperatures on different substrates [12,13]. Fe_3O_4 thin films grown on single crystalline substrates naturally

form antiphase boundaries (APBs) [14,15], which always produce anomalous properties, for instance, a lower Verwey transition temperature (T_V), and the out-of-plane magnetization is smaller than the in-plane magnetization at the same magnetic field, while thin films grown on buffer layers can result in polycrystalline or amorphous phases.

Thermal growth SiO_2 substrates are typical amorphous substrates, which do not provide preferred orientation for films grown on them. Hence, the films grow relaxed, leading to its lattice parameter very close to the bulk value [16]. In this paper, a single crystal Fe_3O_4 thin film with the (111) orientation on a 300nm thermal growth SiO_2 substrate is prepared. Experimental results show that T_V increases to 140 K and can be suppressed by out-plane magnetic field; moreover, the out-plane magnetization is larger than the bulk value and the in-plane magnetization.

The pulsed laser deposition technique (PLD) is an effective method to produce high quality thin films due to the high kinetic energy of atoms and ionized species in the laser-induced plasma. The thin film used was grown on an amorphous SiO_2 substrate using an $\alpha\text{-Fe}_2\text{O}_3$ target, and a 300 nm amorphous SiO_2 substrate is grown on a Si (100) substrate. The target used for the ablation has been prepared by a standard solid-state reaction method. A KrF excimer laser source ($\lambda=248$ nm, pulse width=20 ns) was used to ablate the target at a pulse repetition rate of 10 Hz, and a fluence of $250 \text{ mJ pulses}^{-1}$ was directed at a 45° angle of incidence on the target. The distance from the target to the substrate was maintained at 60 mm during deposition. Before the deposition, the chamber was evacuated to a pressure of 9.9×10^{-6} Pa and the deposition was carried out

at a substrate temperature of 575 °C and in a vacuum of 6×10^{-3} Pa. During the deposition the target was rotated at a rate of 3 rpm to avoid excessive heating and erosion at a single spot on the target surface. At the end of the deposition, the film was cooled down to the room temperature at $3 \text{ }^\circ\text{C min}^{-1}$ in the same environment as used during the deposition.

The structural of the deposited film was characterized by x-ray diffraction (XRD) in θ - 2θ geometry using a Cu K α radiation ($\lambda=1.54059 \text{ \AA}$) (Rigaku, Japan). Phase purity of the film was checked by performing laser Raman spectroscopy. Raman spectra was recorded using a HR800 Jobin-Yvon spectrometer employing He-Ne laser ($\lambda=632.8 \text{ nm}$). The measured resolution of the spectrometer is 1 cm^{-1} . Both XRD and Raman measurements were performed at the room temperature. The film thickness was determined by scanning electron microscope (SEM) and estimated to be 140 nm. The magnetization measurements were carried out using a SQUID vibrational sample magnetometer (SVSM) and the R(T) measurements were performed in standard four-probe geometry using a Quantum Design PPMS.

Figure. 1(a) shows the XRD spectrum of a Fe₃O₄ thin film on a SiO₂ substrate, which clearly suggests that the film is grown with a preferred orientation in the (111) direction. No impurity or peak from other phase of iron oxide peaks is detected from the XRD patterns, suggesting that the film has a pure (111) orientation. The full width at half maximum for the rocking curve of the (111) peak of Fe₃O₄ is 0.1 °, indicating a high degree of orientation quality. Analysis of the XRD peaks shows the presence of the Fe₃O₄ phase in the films. However, the possibility of the presence of γ -Fe₂O₃ cannot be

totally ruled out since they have nearly the same lattice parameters ($a = 0.8397$ nm for Fe_3O_4 ; $a = 0.8342$ nm for $\gamma\text{-Fe}_2\text{O}_3$; and $a = 0.840$ nm for the thin film as calculated from XRD) and all diffraction peaks of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ appear at nearly the same 2θ values.

To confirm the phase purity of Fe_3O_4 in the film, Raman spectroscopy measurements have been performed since the Raman technique is very sensitive to the different phases of iron oxides on account of the vibrational frequencies of different compositions [17]. Figure. 1(b) shows a Raman spectrum of a Fe_3O_4 thin film on a SiO_2 substrate. We can see an acceptable consistency of the $T_{2g}(1)$, $T_{2g}(3)$, $T_{2g}(2)$ and A_{1g} modes corresponding to the Fe_3O_4 phase at 193, 306, 540 and 669 cm^{-1} , respectively. These values are close to that observed in a magnetite single crystal [18]. We note that none of the Raman spectra reveal any signature of the corresponding modes of $\gamma\text{-Fe}_2\text{O}_3$ normally seen at 350, 500, and 700 cm^{-1} . Thus, Raman studies further confirm the pure single phase of our Fe_3O_4 thin film.

Thin films can usually be very different from the bulk materials due to its interaction with the substrate. Here we especially focus on the magnetization properties of the magnetite thin film. Figure. 2 shows the normalized zero-field-cooled (ZFC) and field-cooled (FC) magnetization as a function of temperature with magnetic fields applied parallel and perpendicular to the film plane, respectively. The ZFC spontaneous magnetization curves exhibit a spontaneous magnetization jump in the vicinity of $T_v = 140$ K. Thin films of Fe_3O_4 are known to usually exhibit suppressed T_v ($<120\text{K}$) that could originate from a variety of other reasons, like strain or APB. However, the

measured results on our films show that the transition temperature of Fe_3O_4 is enhanced, which means that there must be an unusual positive coupling between the film and the amorphous SiO_2 substrate. More interestingly, T_V associated with in-plane magnetization is unchanged as the applied field increases, while the transition temperature decreases for out-plane magnetization. The Verwey transition is usually viewed as a charge ordering of the Fe^{2+} and Fe^{3+} in the B sublattice due to local Coulomb correlation U [7-11]. Accordingly, the enhancement of this transition may indicate that the U is strengthened by the interaction with the SiO_2 substrate; and its coupling with the external out-of-plane magnetic field is also unusual, suggesting the charge and spin degrees of freedom are more strongly entangled on our thin film than in the bulk material.

The magnetization hysteresis loops of our thin film also exhibits unconventional behaviour. Figure. 3 shows ZFC magnetization hysteresis loops with magnetic fields parallel and perpendicular to the film plane at different temperatures. We observe that the magnetization of the Fe_3O_4 film is unsaturated at 50 kOe, with a slight residual slope extending to larger magnetic fields. The in-plane hysteresis curves display an almost rectangular shape with higher remanence and smaller coercivity than that of out-of-plane case at the same temperature, indicating that the magnetic moments lie in plane, which is in accordance with the assumption that the easy axis of the films lies in the film plane. The magnetization values measured at 50 kOe field and the coercivities at different temperatures are listed in Table I. At 50 kOe, the out-plane magnetization is about 530 emu cm^{-3} and not saturated even at such a high field at room temperature.

This value is significantly higher than the saturation magnetization of 471 emu cm^{-3} measured at 300 K for bulk Fe_3O_4 . It implies that the film is free from APBs since strong anti-ferromagnetic coupling within APBs reduces the magnetization [19,20]. The enhancement of the saturation magnetization may favour the interpretation that the intrinsic effective ferrimagnetic exchange interaction J is strengthened by the interaction with SiO_2 substrate. Here the enhancement of this effective J may be related to the decreasing of the antiferromagnetic exchanged interaction or increasing of the ferromagnetic exchange interaction of Fe 3d electrons. More unexpectedly, through the comparison of the values of magnetizations with 50 kOe field parallel and perpendicular to the film plane, the out-plane magnetization is even higher than the in-plane magnetization. This is very striking as the shape anisotropy is expected to confine the magnetic moments to the plane of the film; and it implies the existence of unconventional ferrimagnetic coupling anisotropy. Recalling that the Verwey transition can lead to a negative jump of the magnetization while the out-plane magnetic field can suppress the Verwey transition for our film, it may be inferred that the Coulomb correlation and the ferrimagnetic interaction is entangled along c-axis of the film and contribute to their unusual anisotropy.

In summary, the (111) oriented single crystalline Fe_3O_4 thin films have been successfully prepared on amorphous SiO_2 substrates. The Verwey transition temperature is higher than the 120K transition temperature of the bulk material and can be suppressed by the out-of-plane magnetic field; moreover, the out-of-plane magnetization is higher than that of the bulk material and the in-plane magnetization.

These observations indicate that the local Coulomb correlation and ferrimagnetic exchange interaction are both enhanced and out-of-plane directionally coupled by the unconventional interaction between the Fe_3O_4 thin film and the amorphous SiO_2 substrate. Such novel magnetization properties not only have potential application on spintronics, but also offer an exciting platform for future theoretical and experimental investigations on the cooperation or competition behaviors of U and J in this correlated system.

Acknowledgements

This work was supported by grants from Chinese Academy of Sciences (2010Y1JB6), Ministry of Science and Technology of China (2010CB923000, 2011CBA001000, 2011CBA00102, 2012CB821403 and 2013CB921703) and Chinese National Science Foundation (11234014, 11227903, 11004232, 11034011/A0402 and 11274362).

- [1] E. J. W. Verwey, *Nature (London)* **144**, 327 (1939).
- [2] Z. Zhang and S. Satpathy, *Phys. Rev. B* **44**, 13319 (1991).
- [3] V. I. Anisimov, I. S. Elfimov, N. Hamada, and K. Terakura, *Phys. Rev. B* **54**, 4387 (1996).
- [4] Friedrich Walz, *J. Phys.: Condens. Matter* **14**, 285 (2002).
- [5] Igor Žutić, Jaroslav Fabian, and S. Das Sarma, *Rev. Mod. Phys.* **76**, 323 (2004).

- [6] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, *Science* **294**, 1488 (2001).
- [7] J. P. Wright, J. P. Attfield, and P. G. Radaelli, *Phys. Rev. Lett.* **87**, 266401 (2001).
- [8] Horng-Tay Jeng, G. Y. Guo, and D. J. Huang, *Phys. Rev. Lett.* **93**, 156403 (2004).
- [9] Przemysław Piekarczyk, Krzysztof Parlinski, and Andrzej M. Oleś, *Phys. Rev. Lett.* **97**, 156402 (2006).
- [10] D. J. Huang, H.-J. Lin, J. Okamoto, K. S. Chao, H.-T. Jeng, G. Y. Guo, C.-H. Hsu, C.-M. Huang, D. C. Ling, W. B. Wu, C. S. Yang, and C. T. Chen, *Phys. Rev. Lett.* **96**, 096401 (2006).
- [11] J. Schlappa, C. Schüßler-Langeheine, C. F. Chang, H. Ott, A. Tanaka, Z. Hu, M. W. Haverkort, E. Schierle, E. Weschke, G. Kaindl, and L. H. Tjeng, *Phys. Rev. Lett.* **100**, 026406 (2008).
- [12] D. T. Margulies, F. T. Parker, and F. E. Spada, *Phys. Rev. B* **53**, 9175 (1996).
- [13] S. Soeya, J. Hayakawa, H. Takahashi, K. Ito, C. Yamamoto, A. Kida, H. Asano, and M. Matsui, *Appl. Phys. Lett.* **80**, 823 (2002).
- [14] W. Eerenstein, T. T. M. Palstra, S. S. Saxena, and T. Hibma, *Phys. Rev. Lett.* **88**, 247204 (2002).
- [15] S. K. Arora, R. G. S. Sofin, and I. V. Shvets, *Phys. Rev. B*, **72**, 134404 (2005).
- [16] Shailja Tiwari, Ram Prakash, R. J. Choudhary, and D. M. Phase, *J. Phys. D: Appl. Phys.* **40**, 4943 (2007).
- [17] I. Chamritski and G. Burns, *J. Phys. Chem. B* **109**, 4965 (2005).
- [18] R. Gupta, A. K. Sood, P. Metcalf, and J. M. Honig, *Phys. Rev. B* **65**, 104430 (2002).

[19] D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison, and A. E. Berkowitz, *Phys. Rev. Lett.* **79**, 5162 (1997).

[20] W. Eerenstein, T. Hibma, and S. Celotto, *Phys. Rev. B* **70**, 184404 (2004).

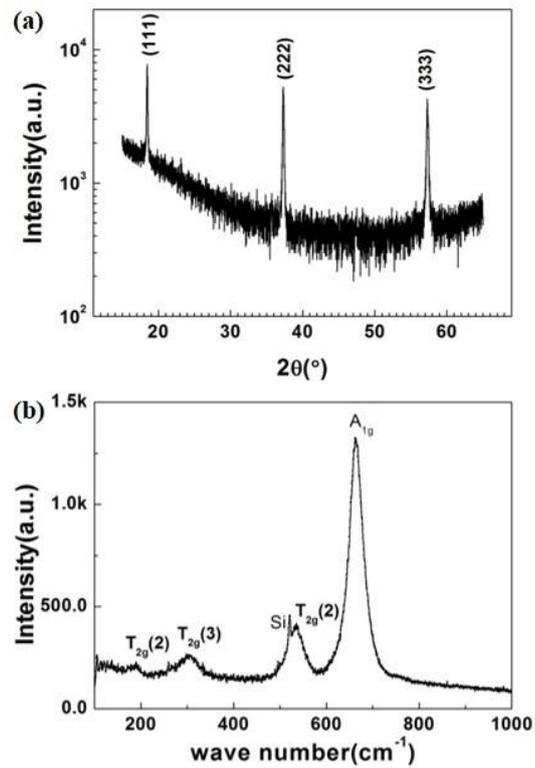


FIG. 1 (color online) (a) XRD spectrum of a Fe_3O_4 thin film on a SiO_2 substrate measured at the room temperature. (b) Raman spectrum of a Fe_3O_4 thin film on a SiO_2 substrate measured at the room temperature.

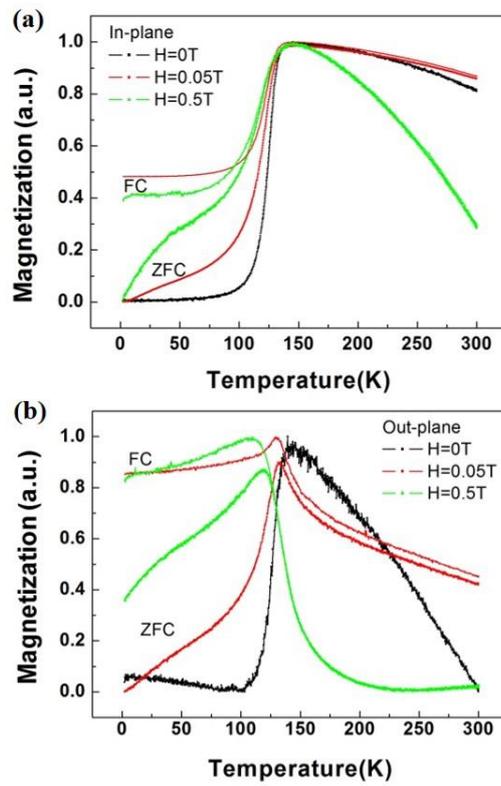


FIG. 2 (color online) Normalized ZFC and FC magnetization as a function of temperature with magnetic fields applied parallel (a) and perpendicular (b) to the thin film plane.

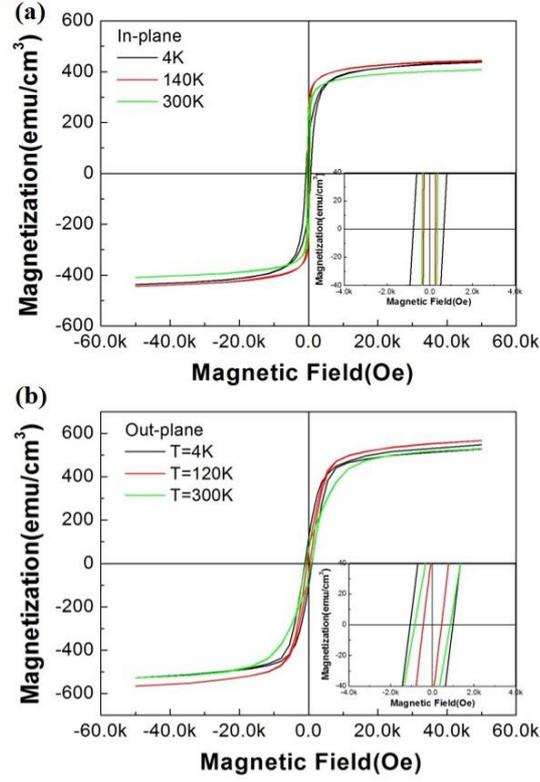


FIG. 3 (color online) Magnetization hysteresis loops measured at 4, 140 and 300 K with an in-plane (a) and out-of-plane (b) magnetic field up to ± 50 kOe. The inset shows the low field magnetization.

		Field	4K	140K	300K
M_{5T} (emu cm^{-3})	In-plane		437	442	409
	Out-plane		528	567	530
H_c (Oe)	In-plane		-766/664	-274/250	-359/359
	Out-plane		-1071/974	-445/432	-847/848

TABLE I. Temperature dependence of M_{5T} and H_c of the Fe_3O_4 film obtained in the H-parallel and H-perpendicular cases with respect to the film plane.