Magnetic anisotropy modulation of magnetite in $\text{Fe}_3\text{O}_4/\text{BaTiO}_3(100)$ epitaxial structures

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Temperature dependent magnetometry and transport measurements on epitaxial $\text{Fe}_3\text{O}_4$ films grown on $\text{BaTiO}_3(100)$ single crystals by molecular beam epitaxy show a series of discontinuities, that are due to changes in the magnetic anisotropy induced by strain in the different crystal phases of $\text{BaTiO}_3$. The magnetite film is under tensile strain at room temperature, which is ascribed to the lattice expansion of $\text{BaTiO}_3$ at the cubic to tetragonal transition, indicating that the magnetite film is relaxed at the growth temperature. From the magnetization versus temperature curves, the variation in the magnetic anisotropy is determined and compared with the magnetoelastic anisotropies. These results demonstrate the possibility of using the piezoelectric response of $\text{BaTiO}_3$ to modulate the magnetic anisotropy of magnetite films.

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Complex oxides are characterized by a range of multifunctional electronic behavior, including magnetism, ferroelectricity, and correlated electron transport phenomena. Recently, much effort has been devoted to controlling these properties by means of external electric and magnetic fields. Besides intrinsic multiferroic materials, which display simultaneous magnetic and electric polarization, new classes of composite materials are being developed that explore the different properties of the individual components to develop systems with larger susceptibilities and more varied response functions. Examples of multiferroic composites include $\text{Fe}_3\text{O}_4/\text{BaTiO}_3$ heterostructures, where a strong bias dependence of the magnetoresistance is observed. Magnetite, $\text{Fe}_3\text{O}_4$, is a complex oxide material with several outstanding properties: it is a ferrimagnetic conductor with a high Curie temperature of $\sim 850$ K and large spin polarization. It is a mixed valence oxide which crystallizes in the cubic inverse spinel structure, with a room temperature lattice constant of 8.397 Å. Here, we exploit the fact that epitaxial $\text{Fe}_3\text{O}_4$ films grown on lattice mismatched substrates develop an extra magnetic anisotropy term due to magnetoelastic coupling. Of potential interest would be the ability to modulate the magnetic anisotropy of magnetite by using the piezoelectric effect of a ferroelectric material, such as $\text{BaTiO}_3$.

$\text{Fe}_3\text{O}_4/\text{BaTiO}_3$, which were attributed to changes in the magnetic domain structure of $\text{Fe}_3\text{O}_4$. In these films the authors suggest the $\text{Fe}_3\text{O}_4$ is compressively strained. In this letter, we show that the magnetic anisotropy of thin $\text{Fe}_3\text{O}_4$ films is modulated by the change in strain associated with the structural phase transitions of $\text{BaTiO}_3$. We demonstrate that at room temperature, the magnetite films are under tensile strain, which is key to understanding the changes in the magnetic anisotropies. We explain the changes in magnetic anisotropy in terms of magnetoelastic coupling and provide numerical estimates for the various $\text{BaTiO}_3$ phases and domains.

$\text{BaTiO}_3$ has a simple cubic perovskite structure between 1733 K and 393 K ($a = 3.996$ Å at 393 K). Between 393 K and 278 K, it is tetragonal and ferroelectric, with lattice constants $a = 3.9920$ Å and $c = 4.0361$ Å (293 K). Below 278 K it converts to an orthorhombic structure ($a = b = 4.013$ Å, $c = 3.99$ Å, $\gamma = 89.869^\circ$, in the monoclinic representation), and below 183 K it undergoes a further transition to a rhombohedral structure ($a = 4.001$ Å, $\gamma = 89.85^\circ$ at $T = 105$ K). In all cases, the lattice can be seen as a slightly distorted cubic structure.

For this study, a 30 nm thick magnetite film was grown on a $\text{BaTiO}_3(100)$ single crystal by molecular beam epitaxy in an ultrahigh vacuum deposition system with a base pressure of $1 \times 10^{-9}$ mbar. Prior to film growth the $\text{BaTiO}_3$ substrate was annealed at 900 K, exhibiting sharp low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED) patterns, as shown in Fig. 1. For the magnetite growth, an atomic Fe beam was thermally generated from an effusion cell under an $\text{O}_2$ partial pressure of $2 \times 10^{-7}$ mbar, with the substrate temperature being held at 570 K. The film thickness was estimated from a calibrated thickness monitor (and corroborated by x-ray reflectivity measurements), while film crystallinity was monitored during growth using RHEED. After growth, the film

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was characterized in situ by LEED and x-ray photoemission spectroscopy (XPS). Ex situ measurements include x-ray diffraction (XRD), atomic force microscopy (AFM), superconducting quantum interference device (SQUID) magnetometry, and resistivity measurements; the BaTiO$_3$ substrate crystal orientation was confirmed by Laue diffraction.

RHEED and LEED patterns indicate that magnetite grows epitaxially on BaTiO$_3$ in the (100) orientation, with Fe$_3$O$_4$(100)[100]||BaTiO$_3$(100)[100]. The RHEED diffraction spots of Fe$_3$O$_4$ broaden compared to those of the BaTiO$_3$ during the early stages of growth, indicating a three-dimensional growth mode. The observation of LEED patterns in the magnetite film indicates a relatively well ordered surface. XPS measurements show the presence of both Fe$^{2+}$ and Fe$^{3+}$, as expected for the mixed valence magnetite. These data rule out the growth of the competing maghemite phase (γ-Fe$_2$O$_3$), also a cubic inverse spinel with $a = 8.322$ Å and indicate that we are able to grow stoichiometric, high quality epitaxial Fe$_3$O$_4$ thin films on BaTiO$_3$. AFM shows that the Fe$_3$O$_4$ surface is relatively smooth, with an average surface roughness of 2 Å over 4 $\mu$m$^2$ scan areas. XRD measurements after sample growth indicate that, in this case, the BaTiO$_3$ contains no $c$ domains (see Fig. 2, and no planes other than the (100) are detected. The peak at $\theta = 43.39^\circ$ is attributed to Fe$_3$O$_4$, giving an out of plane lattice constant of 8.344 Å, smaller than the bulk value (8.397 Å) and at odds with what is expected from the lattice mismatch with BaTiO$_3$(100) of about 4.7%. This result can be explained by assuming that the magnetite film relaxes fully during growth, while the tensile strain results from the lattice expansion of BaTiO$_3$ at the cubic to tetragonal transition at 393 K.

Figure 2 shows the variation of the magnetic moment of magnetite as a function of temperature at zero applied field. We find that at the temperatures corresponding to the phase transitions of BaTiO$_3$, there are large jumps in the Fe$_3$O$_4$ magnetization, which we associate with changes in the domain structure due to strain-induced variations in the magnetic anisotropy. This result demonstrates that we are able to modulate the magnetic response of magnetite via a strain-induced magnetoelastic interaction. Note in particular the large change in magnetization at around 120 K, which is coincident with the vanishing of the magnetocrystalline anisotropy constant at the Verwey temperature of bulk magnetite. The M-H curves at room temperature show that the film is magnetized in-plane, although there is a small non-zero remanence along the out of plane direction, as shown in the inset to Fig. 3. From our data we obtain a saturation magnetization $M_s = 470 \pm 40$ emu/cm$^3$, similar to the bulk value. Resistivity vs temperature measurements (not shown) also reveal the presence of discontinuities at the BaTiO$_3$ phase transitions, which we associate with changes in domain structure and to anisotropic magnetoresistance; a large increase in resistivity by several orders of magnitude at about 120 K compares well with the onset of the Verwey transition, indicating a magnetite film with good stoichiometry.

To study the changes in the magnetic anisotropy more systematically, we measured the variation of the magnetic moment of magnetite as a function of temperature along different crystal directions under a constant magnetic field of 2 kOe, which lies in the reversible part of the M-H curve but below saturation. In this case, changes in the magnetization reflect directly changes in the magnetic anisotropy rather than in the domain structure. The results of the magnetization measurements are shown in Fig. 4, where again we find that at the temperatures corresponding to the phase transitions of BaTiO$_3$, there are abrupt jumps in the magnetization. In particular, the jumps in the two in-plane magnetization curves are in the same direction, increasing at 287 K and decreasing at 192 K, while the out of plane magnetization

FIG. 1: LEED and RHEED patterns of the BaTiO$_3$ substrate and the Fe$_3$O$_4$ film at room temperature. The incident electron beam energy for RHEED is 15 keV, and the RHEED azimuths are with respect to the incident beam direction.

FIG. 2: High resolution $\theta - 2\theta$ XRD measurements (Cu K$_\alpha$) near the (002) scattering plane of BaTiO$_3$. 

FIG. 3: Shows the variation of the magnetic moment of magnetite as a function of temperature at zero applied field.
Magnetization (emu/cm$^3$) vs. Temperature (K)

FIG. 3: Magnetization versus temperature dependence of magnetite along the in-plane [100] direction under no applied field. The Fe$_3$O$_4$ film was initially saturated magnetically at 320 K under a field of 10 kOe. The inset shows room temperature $M$-$H$ loops along different crystal directions, corrected for the diamagnetic contribution from the substrate. The [001] direction is out of plane.

curve has the opposite behavior. This clearly indicates that the changes in anisotropy occur predominantly as a consequence of changes in the out of plane magnetic anisotropy, which is reduced between 287 K and 192 K. We attribute the variation of the magnetic anisotropy observed experimentally at the phase transitions of BaTiO$_3$ to strain-induced magnetoelastic anisotropy, arising from distortions in the crystal structure of the magnetite film.

The magnetic anisotropy can be estimated from the phenomenological expressions for the elastic and magnetoelastic energies, yielding

$$E_{me} = [K_1 \cos 2\phi + K_2 \sin 2\phi] \sin^2 \theta + K_p \cos^2 \theta$$

where $K_1 = b_1(\epsilon_{xx} - \epsilon_{yy})/2$ and $K_2 = b_2 \epsilon_{xy}/2$ correspond to in-plane magnetoelastic anisotropy constants, and $K_p = b_1(1 + c_{11}/2c_{12})\epsilon_{zz}$ is the perpendicular magnetoelastic anisotropy constant. In this expression, $\epsilon_{ij}$ are the strain components, $c_{ij}$ the elastic constants, $b_i$ the magnetoelastic coupling coefficients, $\theta$ and $\phi$ the polar and azimuthal angles of the spherical coordinate system, respectively, with the polar axis along the $z$ direction. For tensile strain, the magnetoelastic interaction in Fe$_3$O$_4$ favors perpendicular magnetic anisotropy ($K_p < 0$), in agreement with our observation of a negative out of plane strain in XRD and the presence of perpendicular magnetic remanence in the $M$-$H$ loops. This result is not expected if a positive (compressive) residual strain were present from the lattice mismatch between Fe$_3$O$_4$ and BaTiO$_3$. In Table I we show our estimates for $K_p$, assuming the experimental strain at 300 K and considering the strain that results from the lattice distortions of the BaTiO$_3$ (we take into account the temperature variation of both BaTiO$_3$ and Fe$_3$O$_4$ lattice constants). Negative $K_p$ favors perpendicular magnetization; these simple calculations suggest that $K_p$ can change by a factor of 4 from the square surface domains of tetragonal BaTiO$_3$ to the oblique surface domains of the orthorhombic phase.

Table I: Calculated values for $10^6\,K_p$ (erg/cm$^3$), for Fe$_3$O$_4$ films strained according to the different phases and domains of the underlying BaTiO$_3$ substrate at 272 K and 187 K.

| T(K) | tetragonal | orthorhombic | rhombohedral |
|------|------------|--------------|--------------|
| 272  | -0.22      | -0.71        | -0.47        | -0.75        | —         |
| 187  | —          | -0.45        | -0.85        | -0.66        |

Thermal cycling of the BaTiO$_3$ crystal during the temperature dependent measurements leads to the formation of different types of domains, for instance, $a$ and $c$ domains in the tetragonal phase, and oblique or rectangular in the orthorhombic phase. These domains give rise to different strains in the magnetite film and to different magnetoelastic anisotropy contributions to the magnetic energy. In the tetragonal phase, rectangular domains result in large perpendicular magnetic anisotropy; in the orthorhombic phase, $K_p$ is strongly reduced for rectangular domains, while it increases slightly in oblique domains. Therefore, the decrease in the perpendicular anisotropy can be explained by a transformation of $c$ domains of the tetragonal phase to similar domains in the orthorhombic phase. At 192 K, the increase in

FIG. 4: Temperature variation of the Fe$_3$O$_4$ magnetization under an applied field of 2 kOe, along different crystallographic directions, as labeled. Measurements were performed during cooling in the sequence [100], [110] and [001]; the latter corresponds to the out of plane direction. Curves have been shifted vertically for convenient data display and substrate diamagnetic contributions have not been removed.

![Temperature variation of the Fe$_3$O$_4$ magnetization](image)
perpendicular magnetic anisotropy is explained by the prevalence of rectangular domains in the orthorhombic phase. It suggests that our BaTiO$_3$ crystal changes from an $a$, $c$ multi-domain state at 300 K, to rectangular below 287 K and oblique below 192 K. We note that the magnetostatic energy (shape anisotropy, which favors in-plane magnetization) of the Fe$_3$O$_4$ film is of the order of $2\pi M_s^2 = 1.39 \times 10^6$ erg/cm$^3$. This value implies that the Fe$_3$O$_4$/BaTiO$_3$ films would remain magnetized in-plane, assuming a uniform strain state; in real films, one may expect large interface strains and larger magnetoelastic anisotropies, which may be at the origin of the observed small perpendicular remanent magnetization.

In conclusion, we show that we are able to grow high quality Fe$_3$O$_4$/BaTiO$_3$ heterostructures by molecular beam epitaxy. A tensile strain is present in the Fe$_3$O$_4$ film at room temperature, which indicates that the film relaxes at the growth temperature due to the large lattice mismatch. We show, based on calculations of the magnetoelastic anisotropy constants, that such tensile strain gives rise to a strong perpendicular magnetic anisotropy, as observed experimentally. The different lattice distortions induced by the phase transition of BaTiO$_3$ lead to strong modifications in the magnetocrystalline anisotropy, manifested by large discontinuities of zero-field and near saturation $M$-$T$ curves, demonstrating magnetic anisotropy modulation of Fe$_3$O$_4$ films via strain coupling to the BaTiO$_3$ substrate. These types of structures may be used to control magnetoelectric devices, such as the on/off state of planar Hall effect devices, or to study the effect of strain on the Verwey transition of magnetite.

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1. M. Fiebig, J. Phys. D: Appl. Phys. 38, R123 (2005).
2. M. Ziese, A. Bollerio, I. Panagiotopoulos, and N. Moutis, Appl. Phys. Lett. 88, 212502 (2006).
3. E. W. Gorter, Proc. IRE 43, 1945 (1955).
4. C. A. F. Vaz, C. H. Ahn, and V. E. Henrich, in Epitaxial ferromagnetic films and spintronic applications, edited by A. Hirohata and Y. Otani (Research Signpost, 2008), in press.
5. M. K. Lee, T. K. Nath, C. B. Eom, M. C. Smoak, and F. Tsui, Appl. Phys. Lett. 77, 3547 (2000).
6. D. Dale, A. Fleet, J. D. Brook, and Y. Suzuki, Appl. Phys. Lett. 82, 3725 (2003).
7. R. V. Chopdekar and Y. Suzuki, Appl. Phys. Lett. 89, 182506 (2006).
8. S. Sahoo, S. Polisetty, C.-G. Duan, S. S. Jaswal, E. Y. Tsymbal, and C. Binek, Phys. Rev. B 76, 092108 (2007).
9. H. F. Tian, T. L. Qu, L. B. Luo, J. J. Yang, S. M. Guo, H. Y. Zhang, Y. G. Zhao, and J. Q. Li, Appl. Phys. Lett. 92, 063507 (2008).
10. M. Adachi, Y. Akishige, T. Asahi, K. Deguchi, K. Gesi, K. Hasebe, T. Hikita, T. Ikeda, M. K. Y. Iwata, T. Mitsui, et al., in Landolt-Börnstein - Group III: Crystal and Solid State Physics, edited by Y. Shiozaki, E. Nakamura, and T. Mitsui (Springer-Verlag, Berlin, 2002), vol. 36A1, p. 67.
11. R. A. Lefever, in Landolt-Börnstein - Group III: Crystal and Solid State Physics, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1970), vol. 4b, p. 65.
12. C. A. F. Vaz (2008), arXiv:0811.2146v1 [cond-mat.mtrl-sci].
13. S. Chikazumi, Physics of Ferromagnetism (Clarendon Press, Oxford, 1997), 2nd ed.
14. Y. Bason, L. Klein, J.-B. Yau, X. Hong, J. Hoffman, and C. H. Ahn, J. Appl. Phys. 99, 08R701 (2006).