Electrical and magnetic properties of $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ thin films



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# Electrical and magnetic properties of $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ thin films

**Gong Wai Leung, Mary E Vickers, Thomas Fix and Mark G Blamire**

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, UK

E-mail: gwl24@cam.ac.uk

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**Abstract**

We report that the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ system forms a solid solution within the composition range $0 \leqslant x \leqslant 0.5$ and a room temperature magnetic semiconductor phase exists at $x = 0.20$. This system shows an anomalous Hall effect and is ferromagnetic with a large moment per Fe ion. The results show that the strong La doping provides sufficient carriers to the system to maintain carrier-mediated ferromagnetism for low Fe doping. Furthermore, the presence of ferromagnetism within this phase space raises the possibility that the conduction, and hence the magnetism, could be electronically controlled.

## 1. Introduction

Magnetic semiconductors are of great interest as they promise tremendous opportunities for the development of new spin electronic device concepts. Great progress has been made since the discovery of the carrier-mediated ferromagnetism in doped GaAs and of its control via electric field [1, 2]. However, the application of carrier-mediated ferromagnetism in semiconductors is constrained by the low Curie temperature of doped GaAs and the absence of a single model which is capable of explaining the observed magnetic properties of wide bandgap materials [3]. Recently, the search for room temperature carrier-mediated ferromagnetism has moved into the field of transition metal oxides following the discovery of magnetism in Co-doped $TiO_2$ [4]. Numerous reports of magnetism in other dilute magnetic doped oxides have followed (for example, Mn–ZnO [5], Mn–$Cu_2O$ [6], Cr–$In_2O_3$ [7], Co–$La_{0.37}Sr_{0.63}TiO_3$ [8] and Fe–$SrTiO_3$ [9]); however, the magnetic properties of such systems have been controversial [10–13]. A principal reason for this controversy is that the equilibrium solubility of magnetic ions is often very low in such oxides and any resulting phase separation would generally lead to the formation of intrinsically magnetic clusters. The common strategy to circumvent this problem is to apply non-equilibrium processes such as low temperature molecular beam epitaxy or pulsed-laser deposition (PLD); however, the effectiveness of this strategy varies immensely, depending on the deposition system or material, and metallic clusters have frequently been identified as the origin of the magnetism.

Several previous papers have reported the properties of Co-doped $La_ySr_{1-y}TiO_3$ but with results which implicate Co clusters in the magnetic properties [8, 14]. The aim of the work reported here was to investigate the magnetism in $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ which appears to form a solid solution across the phase diagram. The electronic structures of the end members of the perovskite $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ system are distinctly different. $La_{0.35}Sr_{0.65}TiO_3$ is an antiferromagnetic strongly correlated metal [15, 16], while $La_{0.35}Sr_{0.65}FeO_3$ is an antiferromagnetic charge-ordered semiconductor showing spin canting [17, 18].

## 2. Experimental methods

$La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ targets were prepared by solid state reaction of $SrCO_3$, $Fe_2O_3$, $La_2O_3$ and $TiO_2$ mixed in the correct molar proportions in a pestle and mortar, and sintered at 1400 °C in air. After repeated grinding and heating, the samples were characterized by x-ray powder diffractometry.

The stoichiometric transfer of the ceramic targets to a thin film was carried out by pulsed-laser deposition (PLD) with a KrF ($\lambda = 248$ nm) excimer laser. Although $SrTiO_3$ (0.3905 nm) has a good lattice mismatch with $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$, $SrTiO_3$ substrates become conducting under low oxygen pressure deposition conditions [23–25]. $LaAlO_3$ (001) (0.7880 nm) as used in this study has a slightly larger lattice mismatch with $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ between 2.7% and 3.2%, but remains insulating under the low oxygen partial pressure.

 

**Table 1.** Summary of results.

| $x$ | Thin film out-of-plane lattice parameter (Å) | Thin film in-plane lattice parameter (Å) | Carrier density ($cm^{-3}$) | $R_{Hall}$ (H) | $R(T)$ | $M_s$ [a] at room temperature ($\mu_{B/Fe}$) |
|---|---|---|---|---|---|---|
| 0 | 3.987(2) | 3.891(3) | $-1.10 \times 10^{21}$ | OHE | Metallic | 0 |
| 0.05 | 3.988(1) | 3.921(2) | $1.20 \times 10^{21}$ | OHE | Metallic | 0 |
| 0.10 | 3.987(1) | 3.916(2) | $8.00 \times 10^{20}$ | OHE and AHE | Metallic | 0.64 |
| 0.20 | 3.995(1) | 3.921(2) | $3.55 \times 10^{20}$ | OHE and AHE | Semiconducting | 0.82 |
| 0.30 | 3.995(1) | 3.911(2) | N/A | N/A | Insulating | 0.56 |
| 0.40 | 3.999(1) | 3.977(2) | N/A | N/A | Insulating | 0.51 |
| 0.50 | 4.009(1) | 3.982(2) | N/A | N/A | Insulating | 0 |

[a] $M_s$ = saturation moment.

The substrates were ultrasonically cleaned in acetone and isopropanol before being loaded into the chamber. The chamber was pumped to a background pressure of $1 \times 10^{-7}$ Torr. The substrate was maintained at 680 °C at a growth rate of 0.75 nm $min^{-1}$. The film was deposited in $5 \times 10^{-3}$ Torr Ar to enhance the conductivity by the introduction of oxygen vacancies and was allowed to cool down to room temperature in vacuum.

The x-ray diffraction data were collected on four-circle diffractometers with a mirror with Cu K$\alpha_{1,2}$ and for several samples were collected on a monochromated high resolution x-ray diffractometer (HRXRD) with only Cu K$\alpha_1$. Profile fitting was carried out on all data to obtain the peak position. The thin film lattice parameters were based on the pseudocubic (002) (003), (004) and (013) reflections.

A vibrating sample magnetometer (VSM) was used to characterize the magnetic property of the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ thin films and care was taken to remove the silver epoxy from the back of the substrate to avoid contamination. The film thickness was estimated by x-ray reflectivity (XRR) and varied between 50 and 60 nm. DC resistivity measurements were carried out with the standard four-probe method in a van der Pauw geometry.

The ordinary Hall effect (OHE) and anomalous Hall effect (AHE) were measured in a van der Pauw geometry at room temperature to minimize the magnetoresistance, which increases with lower temperature. A high current was required to minimize the voltage fluctuation, and the sample was allowed to settle for 5 h prior to measurement to obtain a stable temperature. The measurements were carried out with various current and voltage directions to allow the in-plane and perpendicular magnetization components to be separated. The OHE was subsequently removed by fitting a straight line to the high field data and subtracting the linear background.

## 3. Results and discussions

### *3.1. Structural characterization*

Epitaxial (001) $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ films ($x = 0$, 0.05, 0.20, 0.30, 0.40 and 0.5) were grown by PLD from sintered bulk targets on (001) $LaAlO_3$ (LAO) substrates. X-ray diffraction (figure 1) of the targets implies that the material remains single phase across the entire composition range

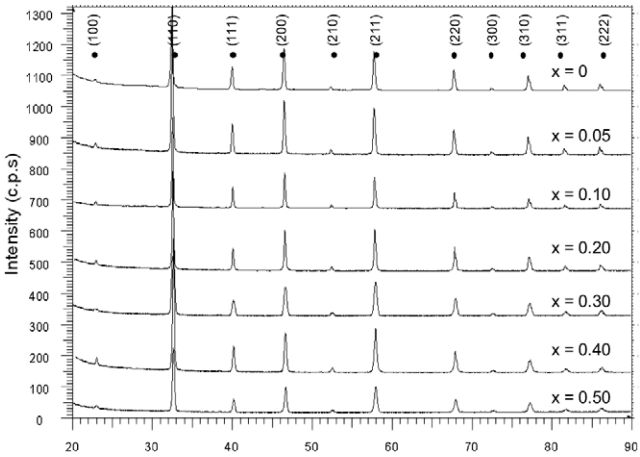


**Figure 1.** XRD $\theta/2\theta$ scan of $La_{0.35}Sr_{0.65}Ti_xFe_{1-x}O_3$ (LSFTO) PLD targets with $x = 0$, 0.05, 0.10, 0.20, 0.30, 0.40 and 0.5.

investigated. This could be expected given the structural similarity of the end members, which minimizes the strain induced in the solid solution and lowers the enthalpy of mixing. Furthermore, similar solid solution systems between Fe and Ti are observed in many minerals including $FeFe_{1-x}Ti_xO_3$ and $SrTi_{1-x}Fe_xO_3$ [9, 19]. The lattice parameters for $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ targets and films are listed in table 1. The in-plane and out-of-plane lattice parameters in the thin film increase with $x$, indicating an overall increase in volume with $x$. Reciprocal space maps indicated that the films were intermediate between fully strained to the substrate and fully relaxed to the pseudocubic structure. In addition, an increase in peak width with increasing Fe content possibly implies an increase in microstrain.

### *3.2. Transport properties*

Figure 2(a) shows the temperature variation of resistance of the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ thin film in the temperature range from 5 K to room temperature for $0 \leqslant x \leqslant 0.20$; for $x \geqslant 0.30$ the samples were insulating. For $x \leqslant 0.10$, the change in resistivity with temperature, $d\rho/dT$, is positive over the entire temperature range, indicating metallic behavior. For $x = 0.20$, $d\rho/dT$ is positive at high temperatures but changes sign, becoming negative around 270 K and remaining negative

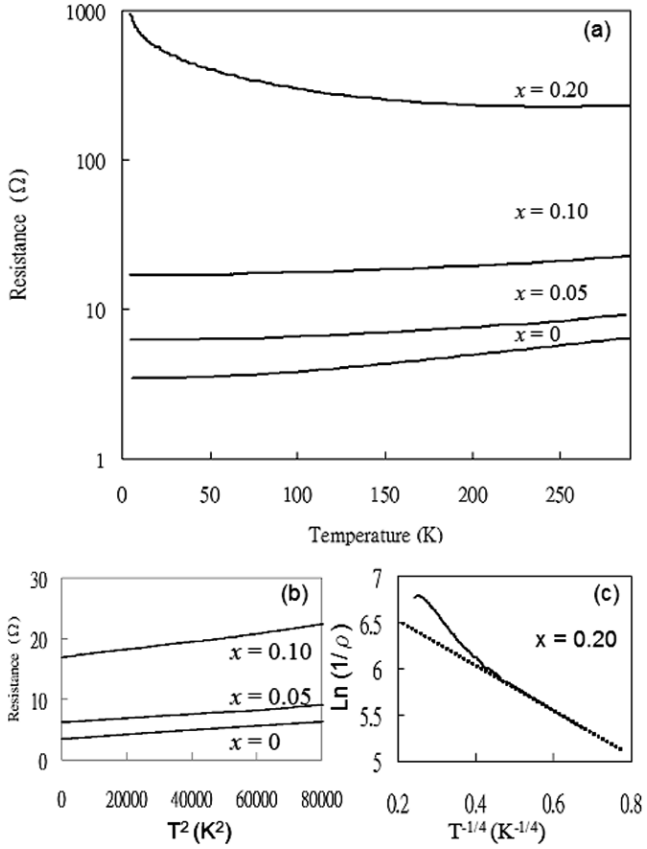


**Figure 2.** Transport properties of $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ (LSFTO) thin film on $LaAlO_3$. (a) Plot of resistance versus temperature of $x = 0$, 0.05, 0.10 and 0.20. (b) Plot of resistance versus $T^2$ of $x = 0$, 0.05 and 0.10. (c) Plot of $\ln(1/\rho)$ versus $T^{-1.4}$ of $x = 0.20$. The dashed line is a guide to the eyes.

for all temperatures below this point. An evaluation of the fit of a theoretical model with experimental data showed that there is evidence for both disorder and electron correlation in the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ system.

The electronic structure of undoped $La_ySr_{1-y}TiO_3$ has been discussed in many papers [15, 16]. The transport data for $x = 0$ shows a $T^2$ dependence of resistance, a negative Hall coefficient which implies an electron-like carrier and a nominal carrier density of $1.1 \times 10^{21}$ cm$^{-3}$ at 300 K: these results are consistent with other reports [20]. For the doped films, $R(T)$ in the metallic region, $x \leqslant 0.10$, can be well expressed up to 300 K by the relation $\rho = \rho_0 + AT^2$ for a wide range of temperatures (figure 2(b)). The $T^2$ dependence of the resistivity is reminiscent of the dominant electron–electron scattering process as observed in metallic $La_{0.35}Sr_{0.65}TiO_3$. There is a gradual decrease in carrier density (see table 1) and an inversion of the sign of the Hall coefficient at $x = 0.05$, implying that the carriers became hole-like when Fe is introduced which is consistent with the Fe being an acceptor dopant on the Ti site.

The temperature dependence of the resistance for $x = 0.20$, which exhibits semiconducting behavior, is shown in figure 2(c). The carrier density is further reduced and the Hall coefficient remains positive. Attempts to fit the observed data to a simple Arrhenius model was unsuccessful, as were those

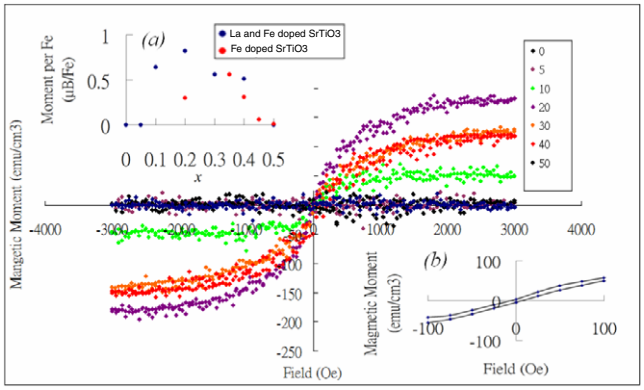


**Figure 3.** Magnetic hysteresis loops at room temperature for the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ (LSFTO) with $x = 0$, 0.05, 0.10, 0.20, 0.30, 0.40 and 0.50 thin films; the background diamagnetic contribution to the magnetization was subtracted. Inset (*a*) shows the plot of moment per Fe ion versus $x$ of Fe doped $SrTiO_3$ [9] and LSFTO. (This figure is in colour only in the electronic version)

based on a small polaron mechanism observed in dilute La-doped $SrTiO_3$. Both $\ln(\rho)$ versus $(1/T)$ and $\ln(\rho/T)$ versus $(1/T)$ plots exhibit no clear linearity from 5 up to 300 K. However, it is well described by the variable range hopping model, $\ln(\rho/\rho_0) = (T_0/T)^{1/4}$ at low temperature. A plot of $\ln\rho$ versus $T^{-1/4}$ is linear in the insulating region, indicating a strongly disordered system with variable range hopping (VRH) which probably originates from disorder associated with the high doping levels and associated Anderson localization. At higher temperatures, $x = 0.20$ becomes metallic, which is indicated by the deviation from the model at high temperature. An abrupt increase in resistance by many orders of magnitude occurs at $x = 0.30$, which indicates a highly insulating sample. It was not possible to measure the $R(T)$ characteristic of the sample at such a high resistance, therefore more experimental work is required to investigate the insulating region.

### *3.3. Magnetic characterization*

Figure 3 shows the out-of-plane magnetic hysteresis loops at room temperature for the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ thin films. No room temperature ferromagnetism is found in the low Fe doping ($x < 0.10$) films in agreement with the findings for dilute Fe-doped Nb:$SrTiO_3$ [21]. To confirm this, we performed a study in which the deposition temperature and oxygen partial pressure were systematically varied for $x = 0.05$, but no ferromagnetism was found down to 5 K.

The films with $0.10 \leqslant x \leqslant 0.40$ all exhibit ferromagnetic behavior with low remanence and coercivity in the VSM characterization. The saturation magnetizations at room temperature for all the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ thin films listed in table 1 are compared in the inset to figure 3 with those of Kim *et al* for $SrFe_xTi_{1-x}O_3$, where for $0.30 \leqslant x < 0.45$ ferromagnetic insulating behavior was observed [9]. At $x = 0.50$, both materials are only minimally magnetic at room temperature which suggests the formation of an ordered antiferromagnetic structure at this composition. Moreover, this seems to be strong evidence against the possibility of Fe clustering as the source of ferromagnetic behavior because

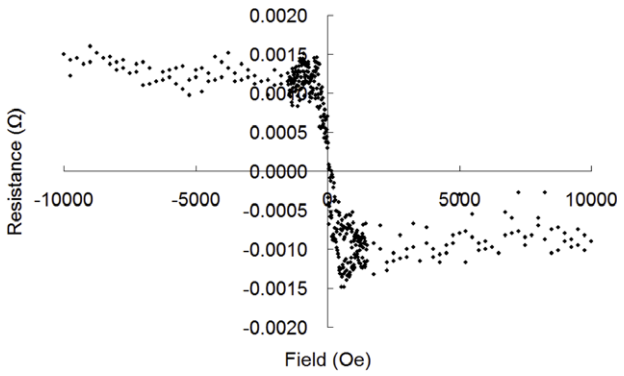


**Figure 4.** Hall measurements at 280 K for the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ (LSFTO) with $x = 0.20$ thin films. The graph shows the anomalous Hall resistance $R_{Hall}$ subtracted by the gradient of the sample as a function of magnetic field at 280 K. The AHE is nonremanent with small hysteresis and the saturation field is approximately 2000 Oe, consistent with the $M(H)$ curve.

$x = 0.50$ would be expected to have the highest magnetic moment if clustering is the origin.

Magnetotransport measurements revealed the occurrence of the anomalous Hall effect (AHE) in the $x = 0.1$ and 0.2 thin film as shown in figure 4. Although AHE is no longer regarded as direct proof of intrinsic ferromagnetism its appearance in a single-phase system is strongly supportive of spin-polarized carriers [14]. It is noted that the AHE is negative and this is sometimes observed in other ferromagnetic oxides such as $La_{1-x}Sr_xMnO_3$ [22].

## 4. Conclusions

We have shown that the $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ system forms a solid solution within the composition range $0 \leqslant x \leqslant 0.5$, and that ferromagnetism appears in all but the end members of the series with an abrupt increase in resistivity at $x \sim 0.3$. There are good grounds for believing that, like $SrTi_{1-x}Fe_xO_3$ [9], this is a system in which the magnetism is not associated with metallic clusters but is intrinsic. For the higher Fe doping levels there is remarkable quantitative agreement between our results with those of Kim *et al* on $SrTi_{1-x}Fe_xO_3$ in which the magnetism has been ascribed to localized $Fe^{3+}$–$O^{2-}$–$Fe^{4+}$ coupling [9]. For $x < 0.3$ $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ differs significantly from $SrTi_{1-x}Fe_xO_3$: the former is conducting, shows an anomalous Hall effect and is ferromagnetic with a large moment per Fe ion, while the latter is insulating and paramagnetic. In this doping regime long-range coupling via superexchange between dopant ions would not be feasible because of the large average Fe–Fe separation and so the presence of magnetism in conducting $La_{0.35}Sr_{0.65}Ti_{1-x}Fe_xO_3$ but not in insulating $SrTi_{1-x}Fe_xO_3$ is strong evidence that the La doping provides sufficient carriers to the system to establish carrier-mediated ferromagnetism for low Fe doping. Finally, the presence of a ferromagnetism within this phase-space raises the possibility that the conduction, and hence the magnetism, could be electronically controlled.

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## References

[1] Ohno H, Shen A, Matsukura F, Oiwa A, Endo A, Katsumoto S and Iye Y 1996 *Appl. Phys. Lett.* **69** 363
[2] Ohno H, Chiba D, Matsukura F, Omiya T, Abe E, Dietl T, Ohno Y and Ohtani K 2000 *Nature* **408** 944
[3] Dietl T 2003 *Nat. Mater.* **2** 646
[4] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 *Science* **291** 854
[5] Sharma P, Gupta A, Rao K V, Owens F J, Sharma R, Ahuja R, Guillen J M O, Johansson B and Gehring G A 2003 *Nat. Mater.* **2** 673
[6] Wei M, Braddon N, Zhi D, Midgley P A, Chen S K, Blamire M G and MacManus-Driscoll J L 2005 *Appl. Phys. Lett.* **86** 072514
[7] Philip J, Punnoose A, Kim B I, Reddy K M, Layne S, Holmes J O, Satpati B, Leclair P R, Santos T S and Moodera J S 2006 *Nat. Mater.* **5** 298
[8] Herranz G, Ranchal R, Bibes M, Jaffres H, Jacquet E, Maurice J L, Bouzehouane K, Wyczisk F, Tafra E, Basletic M, Hamzic A, Colliex C, Contour J P, Barthelemy A and Fert A 2006 *Phys. Rev. Lett.* **96** 027207
[9] Kim H S, Bi L, Dionne G F and Ross C A 2008 *Appl. Phys. Lett.* **93** 3
[10] Coey J M D 2006 *Curr. Opin. Solid State Mater. Sci.* **10** 83
[11] Coey J M D and Chambers S A 2008 *MRS Bull.* **33** 1053
[12] Chambers S A 2006 *Surf. Sci. Rep.* **61** 345
[13] Janisch R, Gopal P and Spaldin N A 2005 *J. Phys.: Condens. Matter* **17** R657
[14] Zhang S X, Yu W, Ogale S B, Shinde S R, Kundaliya D C, Tse W K, Young S Y, Higgins J S, Salamanca-Riba L G, Herrera M, Fu L F, Browning N D, Greene R L and Venkatesan T 2007 *Phys. Rev.* B **76** 085323
[15] Tokura Y, Taguchi Y, Okada Y, Fujishima Y, Arima T, Kumagai K and Iye Y 1993 *Phys. Rev. Lett.* **70** 2126
[16] Hays C C, Zhou J S, Markert J T and Goodenough J B 1999 *Phys. Rev.* B **60** 10367
[17] Takano M and Takeda Y 1983 *Bull. Inst. Chem. Res. Kyoto Univ.* **61** 406
[18] Battle P D, Gibb T C and Lightfoot P 1990 *J. Solid State Chem.* **84** 237
[19] Brown N E, Navrotsky A, Nord G L and Banerjee S K 1993 *Am. Miner.* **78** 941
[20] Vilquin B, Kanki T, Yanagida T, Tanaka H and Kawai T 2004 Effect of Sr doping on $LaTiO_3$ thin films *ICSFS-12: 12th Int. Conf. on Solid Films and Surface (Hamamatsu, June)*
[21] Zhang S X, Ogale S B, Kundaliya D C, Fu L F, Browning N D, Dhar S, Ramadan W, Higgins J S, Greene R L and Venkatesan T 2006 *Appl. Phys. Lett.* **89** 3
[22] Asamitsu A and Tokura Y 1998 *Phys. Rev.* B **58** 47
[23] Herranz G, Basletic M, Copie O, Bibes M, Khodan A N, Carretero C, Tafra E, Jacquet E, Bouzehouane K, Hamzic A and Barthelemy A 2009 *Appl. Phys. Lett.* **94** 3
[24] Fix T, Bali R, Stelmashenko N and Blamire M G 2008 *Solid State Commun.* **146** 428
[25] Siemons W, Koster G, Yamamoto H, Harrison W A, Lucovsky G, Geballe T H, Blank D H A and Beasley M R 2007 *Phys. Rev. Lett.* **98** 4