## Interplay between intrinsic and stacking-fault magnetic domains in bi-layered manganites

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We present a low temperature X-ray photoemission electron microscopy study of the bi-layered manganite compound La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> (BL-LSMO) to investigate the influence of stacking faults, which are structurally and magnetically different from the bi-layered host. In BL-LSMO small magnetic moment persists to  $T^* = 300$ K, well above the Curie temperature of 120K ( $T_C$ ). Our magnetic images show that 3D stacking faults are responsible for the  $T^*$  transition. Furthermore, close to the  $T_C$ , stacking faults are well coupled to the bi-layered host with latter magnetic domains controlling the spin direction of the stacking faults. Contrary to recent reports, we find that stacking faults do not seed magnetic domains in the host via an exchange spring mechanism and the intrinsic  $T_C$  of the BL-LSMO is not lower than 120K.

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Intrinsic properties of complex correlated oxides are extremely susceptible to external perturbations, such as magnetic field, pressure [1] and interfaces with other oxides [2]. The latter situation can naturally occur in classes of layered oxides where regions with different number of transition-metal-oxygen layers exist within the matrix of the layered host material; these intergrowths are known as stacking faults (SF) [3]. Therefore, in these systems, we may have regions with different electronic and magnetic properties from the host, and these SFs have the potential to redefine the host properties. Now, it is generally believed that the cooperative or competitive interactions between intrinsic and extrinsic forces in correlated oxides produce spectacular phenomena such as colossal magnetoresistance (CMR) in manganites. Therefore, to fully understand the behavior of layered correlated oxide systems, we must understand how SFs interact with the host material and influence its intrinsic properties.

The bi-lavered (BL) manganite compound.  $La_{2-2x}Sr_{1+2x}Mn_2O_7$  (BL-LSMO) display very strong CMR effect [4] and are known to contain SFs [3, 5, 6]. These are one of the most investigated manganite compounds with techniques such as angle resolved photoemission spectroscopy (ARPES) [7] and, very recently, it has been shown that SFs can influence the ARPES results [8]. In spite of these developments, questions remain regarding the magnetic behavior of the system. For simplicity, let us focus on the most studied doping level of x = 0.4, La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub>, which has a Curie temperature  $(T_C)$  of 120K. Bulk magnetization measurements on samples, with ~ 0.1% volume fraction of SF, have found two transition temperatures, 120K and 300K [6]. It has been speculated that the magnetization remaining above  $T_C$ , 300K magnetic transition, is due to the existence of SFs and the 120K transition is the intrinsic  $T_C$  of the host BL LSMO [6, 9]. However, more recently, there was a report that intrinsic  $T_C$  for BL-LSMO is around 105K rather than 120K and that the SFs artificially increased  $T_C$  to its generally accepted value [10].

Overall, this gives rise to a number of fundamental



FIG. 1: (Color online) (a) Mn L edge absorption (bottom) and XMCD spectra (top). (b) XMCD amplitude as a function of temperature at 641.5 eV showing two magnetic transitions,  $T_C$  at 120K and  $T^*$  at 300K. The ratio between 300K and 120K jump varies from sample to sample. This is an example of one of the largest ratio.

questions: What is the intrinsic ferromagnetic  $T_C$  of BL-LSMO? Do the BL matrix and the SFs interact magnetically, in particular, can  $\leq 1\%$  volume fraction of SF influence the formation of magnetic domains in the BL host? It is not easy to address these questions due to the lack of a spectro-microscopy technique with magnetic sensitivity that is tuned to the mesoscopic length scales of the SFs. In this letter, we explore these issues using element specific spectro-microscopic evidence.

Single crystals of BL-LSMO  $La_{1,2}Sr_{1,8}Mn_2O_7$  (x = 0.4) were grown by the traveling-solvent float-zone method [9]. X-ray photoemission electron microscopy (X-PEEM) and macroscopic x-ray magnetic circular dichroism (XMCD) experiments were performed at beamlines 11.0.1 (PEEM-3) and 6.3.1, respectively, at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. In both measurements, the samples were cleaved in air immediately before being introduced into the vacuum chamber. It is important to note that Freeland et al. found a monolayer of magnetically dead layer at the surface of a sample that they, like us, cleaved in air [11]. This is not an issue for us because PEEM has a probing depth of  $\sim 5$  to 10 nm and we are able to measure clear magnetic XMCD signal in microscopy and spectroscopy. XMCD measurements were done with fixed helicity circularly polarized x-rays (beam diameter  $\sim 1 \text{ mm}$ ) with an alternating magnetic field of 0.2 T, applied normal to the sample *ab* plane. Full polarization control was available for the PEEM measurements, where the liquid He flow rate into the cryostat was used to control temperature so that no stray magnetic field from an external heater could perturb the system.

The standard (spatially averaged) XMCD and XAS spectra as a function of temperature, with an applied magnetic field of 0.2T, are shown in Fig. 1 (a). While there is strong intensity variation between the XMCD spectra, the lineshape is insensitive to the temperature. Interestingly, as shown in Fig. 1 (b), the XMCD magnitude as a function of temperature drops around 120K  $(T_C)$  and disappears around 300K  $(T^*)$ .  $T_C$  is consistent with the onset of bi-layered ferromagnetism but to find the origin of  $T^*$  we need a spectroscopic technique with spatial resolution, magnetic sensitivity such as Xray photoemission electron microscopy (PEEM).

It is important to note that the XMCD measurements shown in Fig. 1 were performed on a sample chosen for its strong magnetic transition at  $T^*$  compared to that at  $T_C$ , while the following PEEM measurements are done on samples with magnetization curves comparable to Ref. [6], i.e. samples with ~0.1% volume fraction of SF. Fig. 2 (a-d) shows spatially resolved PEEM XMCD images, which are obtained by taking images with left ( $\sigma^+$ ) and right ( $\sigma^-$ ) circularly polarized light and calculating the asymmetry ( $\sigma^+ - \sigma^-$ )/( $\sigma^+ + \sigma^-$ ). Fig. 2 (a) shows an XMCD image at 115K, just below the  $T_C$ , showing large ferromagnetic domains. Just above  $T_C$ , at 121K



FIG. 2: (Color online) (a,b) PEEM XMCD images  $= (\sigma^+ - \sigma^-)/(\sigma^+ + \sigma^-)$  at the Mn L<sub>3</sub>-edge (641.5 eV) at 115 and 121K. (c,d) XMCD images from different regions at 121K. All images are ~ 36 × 36  $\mu$ m. (e) Temperature dependence of the XMCD amplitude from PEEM XMCD images in a region free from SFs showing no magnetic signal above 120K.  $\Delta T$  is used in Fig. 3. (f,g) O K edge spectra taken with E  $\parallel a/b$  (red) and E  $\parallel c$  (blue) in SF and BL region of the sample, integrated over ~ 0.5 × 0.5  $\mu$ m window, at 121K.

(Fig. 2(b)) most of the sample is nonmagnetic but some smaller ferromagnetic regions remain. By moving into other areas on the sample (Fig. 2(c,d)) we have found these surviving patches of ferromagnetism in different sizes and shapes. We will refer them as  $T^*$  domains. We did not find any magnetic signal in  $T^*$  domain areas at 310K  $(T > T^*)$  above 1% noise level. We used our XMCD images taken as a function of temperature in an area free from the  $T^*$  domains to generate a magnetization curve, which is shown in Fig. 2(e). There is an overall monotonic rise of magnetization below  $T_C$  and, most importantly, it is clear that in BL-LSMO regions the remnant magnetization goes to zero above 120K. We can estimate the SF volume fraction from the SF surface area coverage which we found out to be  $\sim 0.15\%$  in an area of  $300 \times 300 \ \mu m^2$ , roughly in agreement with the estimation in Ref. [6]. To summarize, Fig. 2 (a-d) show that  $T^*$  and  $T_C$  are Curie temperatures for difference regions within the sample and we need to perform spatially resolved spectroscopy to find out the difference between these regions.



FIG. 3: A time sequence of XMCD cooling images  $(10 \times 10 \,\mu\text{m})$  show development of the BL domains in the vicinity of  $T_C$  ( $\Delta$ T defined in Fig. 2 (e)) and the interplay between SF and BL ferromagnetic domains.

One of the goals of the spectroscopic studies is to detect structural difference between the  $T^*$  and  $T_C$  regions. Here we present spectroscopic analysis of the oxygen K edge spectra since O atoms hybridize with both La/Sr and Mn sites and therefore carry all the structural anisotropy information whereas Mn atoms are always surrounded by only O sites and therefore only carry indirect structural information. On top of this, O K edge spectra are much easier to interpret since multiplet effects are much less for  $1s \rightarrow 2p$  transitions, unlike  $2p \rightarrow 3d$  transitions (Mn L edge) where 2p and 3d radial wave functions have substantial overlap [12].

We performed spatially resolved spectroscopy with PEEM by tuning the incident photon energy, obtaining a spectrum from every pixel of the image. Fig. 2(f,g) show spectra taken with linearly polarized x-rays with polarization parallel to the ab plane (red spectra) and the caxis (blue) from  $T^*$  domains (f) and BL regions (g) defined by the red and green boxes,  $\sim 0.5 \times 0.5 \,\mu m$  window, in Fig. 2(b), respectively. While Fig. 2(f) shows no difference between the spectra taken with  $\mathbf{E} \parallel a/b$  and  $\mathbf{E} \parallel c$ (to be precise, E,  $30^{\circ}$  away from the c axis), (g) shows a clear difference, especially around 533 eV. This tells us that in-plane (||a/b| axis) and out-of-plane (||c|) axis local electronic environments are different from each other in the majority of the sample, where no magnetic domains are left above  $T_C$ , as expected for a quasi 2D system such as BL-LSMO. However, the in-plane and out-of-plane environments are essentially the same in the  $T^*$  domains. If we compare the spectral features with published X-ray absorption data [13, 14] we see that the 533 eV peak is absent in cubic  $La_{1-x}Sr_xMnO_3$  and present in the  $E \parallel a/b$ spectra on BL-LSMO. Indeed, oxygen (O) peaks in the energy range of 533-536 eV are known to be of La 5d/Sr4d character [15], and (La,Sr)O planes are the main difference between the crystal structure of cubic (3D) and BL-LSMO. Combined with the fact that cubic manganite  $La_{0.6}Sr_{0.4}MnO_3$  (number of layers in Ruddlesden-Popper series,  $n = \infty$ ) has a magnetic  $T_C$  of ~ 350K [1], this is a direct confirmation that  $T^*$  domains have a more 3-dimensional character ( $2 < n \leq \infty$ ) and, therefore, are stacking faults (SF). These results directly connect the magnetic behavior with the dimensionality of the Mn-O network.

So far, we have discussed properties of two seemingly distinct type of magnetic domains. It is an important next step to know if and how they might influence one other. One possible mechanism is exchange spring, where a "hard" magnet controls the magnetization direction of an adjacent "soft" magnet, that is of tremendous interests in modern spin-based electronics [16]. There are theoretical predictions that the required volume fraction of the hard magnet can be as low as 9%, completely enclosed by the soft magnetic material host, to raise the overall coercivity of the composite material (Ref. [16], Fig. 2). Even though these ideas are being extensively explored in metallic multilayers, they are much less explored in correlated oxides, such as manganites.

In this context, it is important to note that Ref. [10] suggests that the intrinsic  $T_C$  of La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> is lower than the measured value of 120K and that this elevated  $T_C$  is due to the influence of higher  $T_C$  SF magnetic domains on the BL domains via an exchange spring mechanism. We consider this hypothesis by direct spatially resolved XMCD imaging of the magnetic domain formation close to 120K, as shown in Fig. 3 (a-f), as the sample is cooled across  $T_C$ . The white region at the center of Fig. 3 (a) is a SF region enclosed by non-magnetic gray BL-LSMO region. The temperature difference between Fig. 3 (a) and (f),  $\Delta T \sim 10$ K, is defined in Fig. 2 (e). First of all, we do not see any change in the size of the SF domains below  $T^*$  and hence can rule out the possibility

that the SFs are seeding domains in the adjacent host BL system via the exchange spring mechanism. Now, in Fig. 3 (b), we note that the BL magnetic domains start to form exactly at 120K. This happens regardless of their proximity to the SF domains. We checked this in several regions of the sample, close to and far from the SF domains, and with different cooling and warming rates. We can also rule out the possibility of BL domains generated by SF underneath the top layer because the average size of the SFs is about  $1 \times 1 \,\mu m$  (SFs in Fig. 2 (c,d) are some of the largest we found within an area of  $\sim 200 \times 200 \,\mu m$ ) and the average size of BL domains are always larger than tens of microns. By comparing with Fig. 1 where the sample has a higher volume fraction of SF, we can conclude that BL  $T_C$  is also independent of the SF concentration. This confirms that the intrinsic  $T_C$  of La<sub>1.2</sub>Sr<sub>1.8</sub>Mn<sub>2</sub>O<sub>7</sub> is indeed 120K, not lower and is not driven by coupling to the SFs.

As the images in Fig. 3 (b-d) show, the BL domain structure fluctuates very close to  $T_C$ . Something very interesting happens between (d) and (f). At this point, we should note that the SF region at the center of the frames is actually a composite structure of two grains. In (e), as a BL domain wall moves across the top SF grain, the spin direction of the grain flips following that of the surrounding BL domain. This continues in (f) with the BL domain completely enclosing both of the SF grains and thereby flipping the spin direction of both. Overall, contrary to expectations, SFs do not act as pinning sites for the BL domains; instead they follow orders from the host, which spontaneously becomes ferromagnetic at 120K. The coupling between SF and BL can be either due to strong exchange between SF and BL spins or to the dipolar interaction driven by the much larger number of spins, and hence bigger internal field (H), provided by the local BL domain.

To summarize, the intrinsic  $T_C$  of BL-LSMO is indeed 120K, not lower. There is strong cooperation between the two structurally and electronically different regions at  $T_c$  and higher  $T_C$  SF magnetism follow the spin direction of the surrounding BL magnetic domains. Many other compounds in the Ruddlesden-Popper series, such as cuprates and ruthenates, may have SFs in them and a thorough PEEM study on a broader class of materials is needed to find the general influence of SFs on the spectacular electronic properties of these intriguing materials.

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- E. Dagotto, Nanoscale Phase Separation and Colossal Magnetoresistance, Springer, Berlin (2003).
- [2] J. Mannhart, and D.G. Schlom, Science **327**, 1607 (2010).
- [3] J. Sloan, P.D. Battle, M.A. Green, M.J. Rosseinsky, and J.F. Vente, J. Solid State Chem. 138, 135 (1998).
- [4] Y. Moritomo, A. Asamitsu, H. Kuwahara, and Y. Tokura, Nature 380, 141 (1996).
- [5] R. Seshadri, M. Hervieu, C. Martin, A. Maignan, B. Domenges, B. Raveau, and A.N. Fitch, Chem. Mater. 9, 1778 (1997).
- [6] C.D. Potter, M. Swiatek, S.D. Bader, D.N. Argyriou, J.F. Mitchell, D.J. Miller, D.G. Hinks, and J.D. Jorgensen, Phys. Rev. B 57, 72 (1998).
- [7] Y.-D. Chuang, A.D. Gromko, D.S. Dessau, T. Kimura, and Y. Tokura, Science **292**, 1509 (2001); N. Mannella, W.L. Yang, X. J. Zhou, H. Zheng, J. F. Mitchell, J. Zaanen, T. P. Devereaux, N. Nagaosa, Z. Hussain, and Z.-X. Shen, Nature **438**, 474 (2005); Z. Sun, J.F. Douglas, A.V. Fedorov, Y.-D. Chuang, H. Zheng, J.F. Mitchell, and D.S. Dessau, Nature Physics **3**, 248 (2007); C. Jozwiak, J. Graf, S.Y. Zhou, A. Bostwick, Eli Rotenberg, H. Zheng, J.F. Mitchell, and A. Lanzara, Phys. Rev. B **80**, 235111 (2009).
- [8] F. Massee, S. de Jong, Y. Huang, W.K. Siu, I. Santoso, A. Mans, A.T. Boothroyd, D. Prabhakaran, R. Follath, A. Varykhalov, L. Patthey, M. Shi, J.B. Goedkoop, and M.S. Golden, Nature Physics 7, 978 (2011).
- [9] J.F. Mitchell, D.N. Argyriou, J.D. Jorgensen, D.G. Hinks, C.D. Potter, and S.D. Bader, Phys. Rev. B 55, 63 (1997).
- [10] G. Allodi, M. Bimbi, R. De Renzi, C. Baumann, M. Apostu, R. Suryanarayanan, and A. Revcolevschi, Phys. Rev. B 78, 064420 (2008).
- [11] J.W. Freeland, K.E. Gray, L. Ozyuzer, P. Berghuis, E. Badica, J. Kavich, H. Zheng, and J.F. Mitchell, Nature Materials 4, 62 (2005).
- [12] F. de Groot, Coordination Chem. Rev. 249, 31 (2005).
- [13] O. Toulemonde, F. Millange, F. Studer, B. Raveau, J.-H. Park, and C.-T. Chen, J. Phys. Cond. Mat. 11, 109 (1999).
- [14] J.H. Park, T. Kimura and Y. Tokura, Phys. Rev. B 58, R13330 (1998).
- [15] M. Abbate, F.M.F. de Groot, J.C. Fuggle, A. Fujimori, O. Strebel, F. Lopez, M. Domke, G. Kaindl, G.A. Sawatzky, M. Takano, Y. Takeda, H. Eisaki, and S. Uchida, Phys Rev B 46, 4511 (1992).
- [16] E.F. Kneller, and R. Hawig, IEEE Trans. Magn. 27, 3588 (1991).