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Exchange bias coupling of Co with ultrathin $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ films

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Magnetic properties of epitaxially grown ultrathin $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO) films down to a thickness of one unit cell (u.c.) have been systematically investigated by studying their magnetic behaviors with Co capping layers. For LSMO thickness below 3 u.c., the Co/LSMO bilayers exhibit strong exchange bias (EB) effects after field cooling, suggesting the existence of antiferromagnetic (AFM) phase at the interfaces in ultrathin LSMO. The presence of exchange bias effect for the bilayer with 1 u.c. thick LSMO further demonstrates that the AFM ordering of the LSMO is C-type AFM ordering structure. For 10 u.c. LSMO, the magnetic properties are clearly not altered by the capping Co film, suggesting that the observed phenomena are caused by the intrinsic properties of LSMO. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4754594>]

Understanding the magnetic and electronic properties of the interfaces created between two different perovskite oxides have gained significant attention in recent years, due to their interesting physics as well as potential application in oxide-based electronic devices. Many unexpected phenomena, such as two-dimensional (2D) high mobility electron gas, 2D superconductivity, and interfacial ferromagnetism have been discovered in those interfaces.^{1–3} The interfacial effects also play a particularly important role in the performance of many devices, e.g., magnetic tunnel junctions (MTJs) and multiferroic memory devices.^{4,5} An important case is the MTJs of $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$ (LSMO)/ SrTiO_3 (STO)/LSMO, of which the tunneling magnetoresistance (TMR) is in excess of 1800% at low temperature.^{4,6} The observed TMR, however, dramatically decreases even when the temperature is far below the Curie temperature, T_C , of LSMO, suggesting the presence of a so-called “dead-layer,” i.e., a layer with depressed magnetization and insulating properties at LSMO/STO interface.⁷ The “dead-layer” is widely observed in many systems and the thickness depends on both the oxide films and the insulating substrates. For LSMO, it is ~ 4 nm on STO (001), ~ 3 nm on NdGaO_3 (110), and ~ 5 nm on LaAlO_3 (001).^{7,8}

Because the electronic and magnetic properties of the interfaces between two oxides are sensitive to epitaxial strain,⁹ broken symmetry,¹⁰ oxygen stoichiometry,¹¹ growth orientation,¹² and polarity discontinuity,^{1–3} the physics of such systems is quite complex and still not well understood. For example, the spin state of “dead-layer” remains controversial, partially owing to the difficulty to characterize their properties, particularly for film thickness down to one or two unit cells (u.c.). Transport and magnetic measurements have shown the presence of spin canting state in the “dead-layer.”¹³ Low-temperature magnetic force microscopy suggested the phase-segregated state of ferromagnetic (FM) metal and charge-ordered insulating phases, driven by nonuniform distribution of strain localized at interface.¹⁴ In particular, using x-ray magnetic linear dichroism (XMLD) to measure LSMO down to 5–6 u.c., some authors reported a preferential e_g ($3z^2-r^2$)

out-of-plane orbital occupation at LSMO/STO interface, suggesting a C-type antiferromagnetic (AFM) phase.^{9,15} However, using the same experimental technique, Huijben *et al.* have shown an opposite result of a preferential e_g (x^2-y^2) in-plane orbital ordering.⁷ For the characterization of AFM phases, polarized neutron reflectivity is probably one of the best techniques.¹⁶ It is, however, hard to measure ultrathin film with the thickness down to a few unit cells.

In order to determine the magnetic state of LSMO dead layer, here, we utilize the exchange bias (EB) effects, which generally occur between ferromagnets and ferrimagnets, antiferromagnets, and spin glasses.^{17,18} The exchange coupling through the interface gives rise to a unidirectional shift in the magnetic hysteresis loop as well as an increase of the magnetic coercivity for the FM layer. In this work, we deposited a very thin layer of Co on ultrathin LSMO films epitaxially grown on STO(001) substrates. We observed strong EB effects and coercivity enhancement for LSMO thicknesses below 3 u.c. (~ 0.4 nm/u.c.). The ferrimagnetic ordering and spin glass phase are ruled out at the interface of LSMO/STO in LSMO by the magnetization measurements, suggesting the presence of AFM. The EB effects rapidly disappear with increasing temperature. For 10 u.c. thick LSMO, Co/LSMO and uncoated LSMO show similar magnetic behaviors, indicating LSMO properties are not modified by Co capping layer and the exchange bias effect is not caused by the oxidation of the Co. Furthermore, the observation of EB down to 1 u.c. LSMO demonstrates the C-type AFM ordering structure other than A-type. The EB effects provide an easy way to study the magnetic states of ultrathin oxide films.

Epitaxial LSMO films were grown on TiO_2 -terminated STO (001) substrates using pulsed laser deposition by applying a KrF excimer laser at a repetition of 2 Hz and a laser fluence of ~ 2 J/cm². The sample growth temperature and oxygen pressure were 750 °C and 1×10^{-5} Torr, respectively. The growth was monitored *in situ* by reflection high-energy electron diffraction (RHEED) and the film thickness was controlled at single atomic level by the intensity oscillations of the RHEED spot. After the film growth, the substrate heater was immediately turned off to quench the sample to room temperature,

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which was demonstrated to help the growth of high quality LSMO films.¹⁹ Then, the LSMO films were transferred into another vacuum chamber of base pressure of 7×10^{-8} Torr without breaking vacuum to deposit Co and the capping layers. The deposition rate of Co was 1.2 nm/min, monitored by a quartz thickness monitor. After less than 5 min, a capping layer of 100 nm tris (8-hydroxyquinolinolato) aluminum III (Alq₃) organic film was deposited to prevent the oxidation of Co films. The magnetic measurements were carried out with the magnetic field applied within the film plane and along the (100) direction of STO using the superconducting quantum interference device (SQUID) magnetometer.

The lattice constants of LSMO and STO are 0.387 and 0.390 nm, respectively. This small lattice mismatch allows epitaxial growth of LSMO, manifested by the same RHEED patterns of LSMO films and STO. The RHEED patterns of LSMO films keep the same at growth temperature and room temperature, indicating the preservation of the structure after cooling from growth temperature. Clear RHEED oscillations are observed [inset of Fig. 1(a)], suggesting layer-by-layer

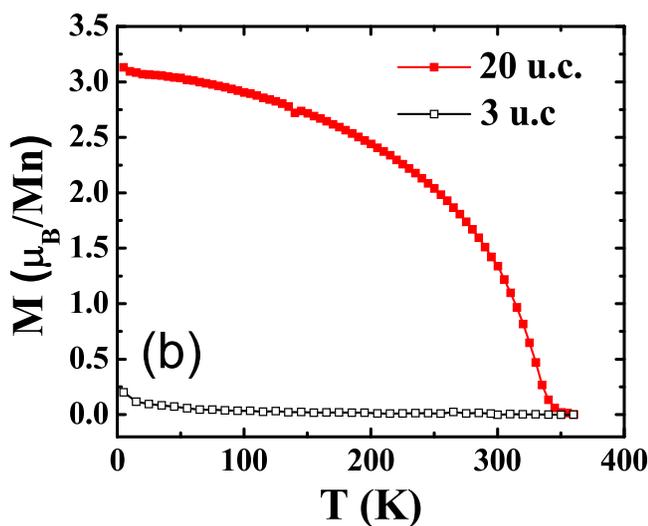
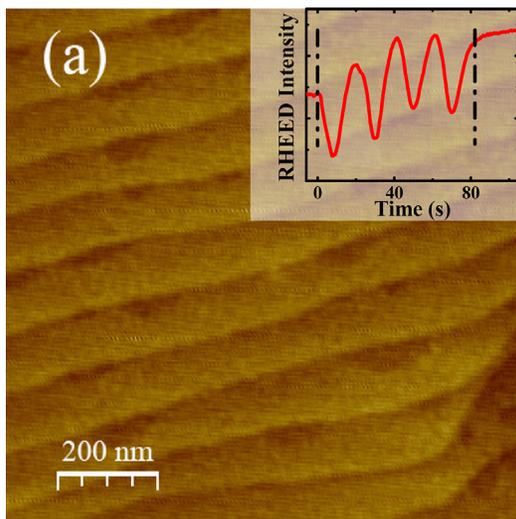


FIG. 1. (a) AFM micrograph of 4 u.c. LSMO, showing a clear step-and-terrace surface. The inset is RHEED intensity as a function of time for growth of 4 u.c. LSMO. (b) Temperature dependence of the magnetization of bare LSMO films with thickness of 3 u.c. and 20 u.c., respectively.

growth, consistent with earlier study.^{7,19} The RHEED oscillations should be absent in step-flow growth and the amplitude of RHEED oscillations should remain constant in ideal layer-by-layer growth with a periodic variation of the roughness. The change of oscillation amplitude may represent the variation of the roughness. We observe a gradual increase of background of the RHEED oscillation, which needs further simulation to understand and is also observed in previous work on LSMO and LaAlO₃ grown on STO substrates.^{1,19} Furthermore, Fig. 1(a) shows a typical surface morphology of ultrathin LSMO films, measured by *ex situ* atomic force microscopy at room temperature. The atomically flat terraces and 1 u.c. step height resemble the surface of the STO substrate, confirming the layer-by-layer growth and suggesting that one period of RHEED oscillation corresponds to 1 u.c. thick LSMO.

In Fig. 1(b), we display the field-cooled (FC) magnetization as a function of the temperature for bare LSMO film with thickness of 3 and 20 u.c. under a magnetic field of 100 Oe. For 3 u.c. film, the ferromagnetism is almost completely depressed, which is consistent with recent reports,⁷ ruling out the possibility of ferrimagnetic ordering. In contrast to 3 u.c. film, the 20 u.c. film clearly exhibits FM order up to 340 K, which is in agreement with Ref. 7 and close to the Curie temperature of bulk LSMO (~ 370 K). Since the T_C of LSMO is sensitive to oxygen stoichiometry,⁷ the fact that T_C of 20 u.c. thick LSMO is close to T_C of bulk LSMO infers that the oxygen stoichiometry of LSMO is almost O₃. Moreover, the magnetizations of LSMO as a function of temperature under zero-field-cooling and field-cooling conditions for both samples show similar curve, suggesting that LSMO is not spin glass state.

The magnetic properties of depositing an ultrathin Co layer on top of LSMO films are subsequently investigated. Fig. 2 shows the magnetic hysteresis loops of a Co (2 nm)/LSMO (2 u.c.) bilayer, which were measured at 5 K after the sample was cooled down from 300 K to 5 K in a magnetic field of 10 kOe and -10 kOe, respectively. Obviously, the center of the loops is shifted away from zero-field and to the opposite direction with respect to the cooling field. This loop

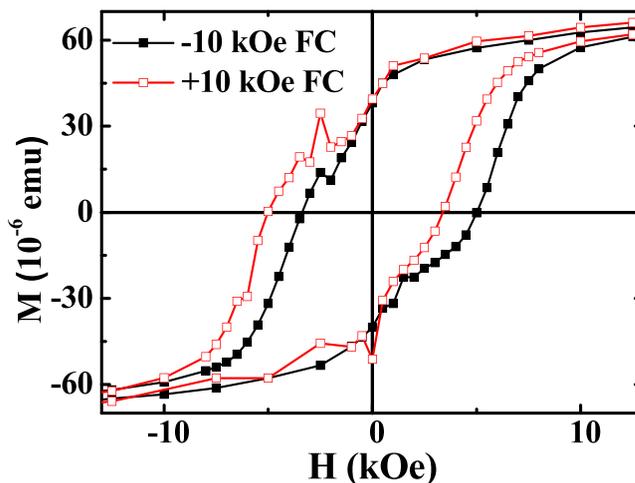


FIG. 2. Magnetic hysteresis loops measured at 5 K after ± 10 kOe FC, respectively. The loops are shifted toward the opposite direction of the cooling field.

shift phenomenon is a classical EB behavior due to the exchange coupling between ferromagnets and ferrimagnets, antiferromagnets, and spin glasses. Since the ferrimagnetic ordering and spin glass phase are ruled out, the EB effect suggests that the AFM phase appears in LSMO. The phase separation between a FM phase and an AFM phase was proposed in thin manganite films.¹⁴ We cannot exclude the nonexistence of FM phase from this measurement. In addition, the pinned uncompensated moments can lead to EB effects.¹⁸ Although a measurable vertical shift in hysteresis loop is not observed, this possibility cannot be ruled out. The EB field, $H_{EB} = (H_{C+} - H_{C-})/2$, where H_{C+} and H_{C-} are the absolute value of coercive field of increasing and decreasing branch of the hysteresis loop, respectively, is about 820 Oe. Moreover, the AFM phase is able to hinder the FM rotation through exchange coupling to enhance the coercive field, $H_C = |H_{C+} + H_{C-}|/2$. Indeed, H_C increases about seven times as compared to that of the same thickness Co film grown on much thicker LSMO with FM state [Fig. 4(b)], which also supports the presence of AFM phase in ultrathin LSMO films.

The magnetic properties of LSMO ultrathin films may be modified if they are in contact with other metals and insulating materials, probably due to interface reaction, interface doping and electrostatic screening effects.^{20,21} Therefore, Co layer may modify LSMO magnetic properties and lead to EB effects. In order to rule out this possibility, we performed the magnetic characterization by SQUID on LSMO (10 u.c.) and Co (2 nm)/LSMO (10 u.c.), shown in Fig. 3. The temperature dependent magnetization of Co/LSMO bilayers exhibits a similar trend with that of LSMO. After the magnetic contribution of Co is subtracted, which is separately measured on Co (2 nm)/STO (001), the data, red triangle symbols in Fig. 3, are almost identical to that of LSMO, demonstrating that the Co layer has no detectable impact on the LSMO. In contrast, a dramatic reduction of T_C and a lower saturation magnetization for about 10 u.c. thick LSMO was observed by capping a Au layer.²¹ Therefore, we conclude that the

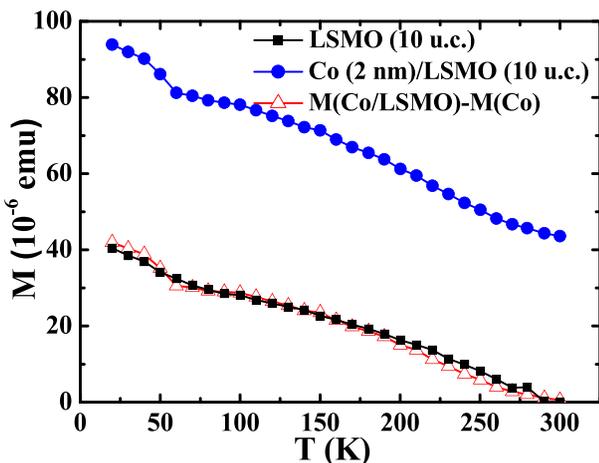


FIG. 3. Temperature dependence of the magnetization of 10 u.c. LSMO film with and without 2 nm Co capping layer, respectively. The diamagnetic contribution from SrTiO₃ substrate has been subtracted. The red triangle symbols are obtained from the magnetization of 10 u.c. LSMO capped with 2 nm Co minus the magnetic contribution of Co capping layer (The magnetization of Co was measured from a Co (2 nm)/STO (001) sample.).

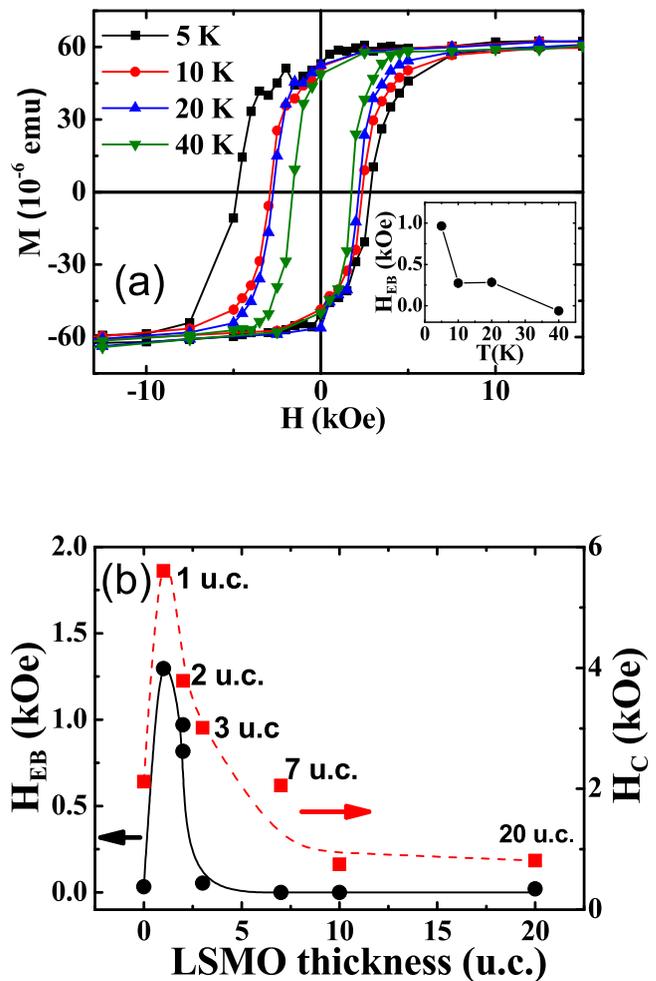


FIG. 4. (a) Magnetic hysteresis loops of Co (2 nm)/LSMO (2 u.c.) bilayers measured at different temperatures. The inset shows the exchange bias field as a function of temperature. (b) Exchange bias field H_E and coercive field H_C as a function of LSMO thickness with 2 nm Co capping layer. The lines are guide to the eyes.

observed EB effect is caused by the intrinsic properties of ultrathin LSMO. We note that magnetic properties of Co/LSMO bilayers are dramatically modified by depositing Al as capping layer, but not by the organic capping layer, due to magnetic properties of Co strongly altered by the extensive intermixture between Al and Co films.²²

Fig. 4(a) shows hysteresis loops of another sample Co (2 nm)/LSMO (2 u.c.) bilayer at different temperatures after 10 kOe FC from 300 K. The temperature dependence H_{EB} has been summarized in the inset of Fig. 4(a). We can find that H_{EB} decreases rapidly with increasing temperature, accompanied by the decrease of H_C . This implies that the AFM/FM exchange interaction is responsible for the enhancement of H_C . And H_{EB} is almost zero when the temperature is approaching 40 K, representing the Néel temperature of AFM phase. This is much lower than the Néel temperature of CoO, suggesting that the EB effects are not caused by CoO.

The LSMO thickness dependence of H_{EB} and H_C for Co (2 nm)/LSMO at 5 K is presented in Fig. 4(b). The EB effects are only observed for 1 and 2 u.c. LSMO. This provides an estimation of AFM layer of about 2 u.c., which agrees with previous report of the critical FM thickness of 3 u.c.,⁷ and implies that the AFM phase only exists at the interface

region. On the other hand, H_C gradually decreases with increasing LSMO thickness, even though EB disappears, and are nearly constant for thickness above ~ 7 u.c., which is about the upper limit of the dead layer.⁷ This could be interpreted in terms of phase separation between FM and AFM. As increasing LSMO thickness, the increase of carrier density weakens the superexchange AFM interaction and enhances the double-exchange FM interaction between Mn ions, leading to phase separation between a FM phase and an AFM phase, as suggested by recent theoretical and experimental study.^{7,11,23} This decreases AFM interaction and shrinks the AFM phase region, resulting in the reduction of AFM anisotropy. For a weaker AFM anisotropy, AFM phase is not sufficiently strong to bias the hysteresis loop, but it can hinder the magnetization rotation of Co and enhance its coercivity. Therefore, the H_C enhancement reflects the existence of AFM phase. Since FM phase is clearly developed for thickness above 3 u.c. [Fig. 1(b)],⁷ our results suggest a distinct electronic phase separation in thickness range of 3 u.c. and ~ 7 u.c. Moreover, the disappearance of EB for LSMO well above the dead layer thickness excludes the possibility that the Co drags oxygen from LSMO to form AFM CoO and hence results in EB effects.

The AFM ordering structure in ultrathin LSMO/STO (001) films is currently under debate. A-type and C-type AFM structures are both proposed based on XMLD experiments.^{7,9,15} In their experiments, they can only detect LSMO thickness above 3 u.c., due to the limited sensitivity of this technique. LSMO thickness dependent EB effects may provide complementary evidence and insight into the AFM structure. From an atomic moment picture, A-type and C-type AFM ordering of 1 u.c. (001) plane is FM and AFM, respectively. Therefore, EB can only be caused by one unit cell thick C-type antiferromagnet, but not by A-type antiferromagnet. Based on this scenario, we believe that the LSMO at the surface region is C-type AFM.

In summary, we utilize a Co capping layer as a probe to investigate the magnetic properties of the ultrathin LSMO films deposited on STO (001) substrates. The Co/LSMO bilayers show a strong EB effect and enhanced coercivity for the LSMO thickness below 3 u.c., suggesting an AFM ordering at the interfaces. With excluding the AFM order from the Co capping layer, the AFM phase for LSMO thickness below 3 u.c. is demonstrated. The fact that the exchange bias effect can be observed for the LSMO layer down to 1 u.c. suggests the AFM structure of ultrathin LSMO film is C-type. The coercivity enhancement of the Co layer is found for the bilayers with the LSMO thickness of 3–7 u.c., indicating

the existence of an AFM phase originated from the phase separation between a FM phase and an AFM phase.

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- ¹A. Ohtomo and H. Y. Hwang, *Nature (London)* **427**, 423 (2004).
- ²A. Brinkman, M. Huijben, M. Van Zalk, J. Huijben, U. Zeitler, J. C. Maan, W. G. Van Der Wiel, G. Rijnders, D. H. A. Blank, and H. Hilgenkamp, *Nature Mater.* **6**, 493 (2007).
- ³N. Reyren, S. Thiel, A. D. Caviglia, L. Fitting Kourkoutis, G. Hammerl, C. Richter, C. W. Schneider, T. Kopp, A.-S. Rüetschi, D. Jaccard, M. Gabay, D. A. Muller, J.-M. Triscone, and J. Mannhart, *Science* **317**, 1196 (2007).
- ⁴M. Bowen, M. Bibes, A. Barthélémy, J.-P. Contour, A. Anane, Y. Lemaître, and A. Fert, *Appl. Phys. Lett.* **82**, 233 (2003).
- ⁵M. Gajek, M. Bibes, S. Fusil, K. Bouzehouane, J. Fontcuberta, A. Barthélémy, and A. Fert, *Nature Mater.* **6**, 296 (2007).
- ⁶R. Werner, A. Yu. Petrov, L. Alvarez Miño, R. Kleiner, D. Koelle, and B. A. Davidson, *Appl. Phys. Lett.* **98**, 162505 (2011).
- ⁷M. Huijben, L. W. Martin, Y.-H. Chu, M. B. Holcomb, P. Yu, G. Rijnders, D. H. A. Blank, and R. Ramesh, *Phys. Rev. B* **78**, 094413 (2008).
- ⁸J. Z. Sun, D. W. Abraham, R. A. Rao, and C. B. Eom, *Appl. Phys. Lett.* **74**, 3017 (1999).
- ⁹C. Aruta, G. Ghiringhelli, V. Bisogni, L. Braicovich, N. B. Brookes, A. Tebano, and G. Balestrino, *Phys. Rev. B* **80**, 014431 (2009).
- ¹⁰H. Zenia, G. A. Gehring, G. Banach, and W. M. Temmerman, *Phys. Rev. B* **71**, 024416 (2005).
- ¹¹S. Brivio, C. Magen, A. A. Sidorenko, D. Petti, M. Cantoni, M. Finazzi, F. Ciccacci, R. De Renzi, M. Varela, S. Picozzi, and R. Bertacco, *Phys. Rev. B* **81**, 094410 (2010).
- ¹²J. X. Ma, X. F. Liu, T. Lin, G. Y. Gao, J. P. Zhang, W. B. Wu, X. G. Li, and J. Shi, *Phys. Rev. B* **79**, 174424 (2009).
- ¹³M. Izumi, Y. Ogimoto, Y. Okimoto, T. Manako, P. Ahmet, K. Nakajima, and T. Chikyow, and Y. Tokura, *Phys. Rev. B* **64**, 064429 (2001).
- ¹⁴A. Biswas, M. Rajeswari, R. C. Srivastava, T. Venkatesan, R. L. Greene, Q. Lu, A. L. de Lozanne, and A. J. Millis, *Phys. Rev. B* **63**, 184424 (2001).
- ¹⁵A. Tebano, C. Aruta, S. Sanna, P. G. Medaglia, G. Balestrino, A. A. Sidorenko, R. De Renzi, G. Ghiringhelli, L. Braicovich, V. Bisogni, and N. B. Brookes, *Phys. Rev. Lett.* **100**, 137401 (2008).
- ¹⁶F. Ott, *J. Phys. Condens. Matter* **20**, 264009 (2008).
- ¹⁷J. Nogués and I. K. Schuller, *J. Magn. Magn. Mater.* **192**, 203 (1999).
- ¹⁸J. de la Venta, M. Erekhinsky, S. Wang, K. G. West, R. Morales, and I. K. Schuller, *Phys. Rev. B* **85**, 134447 (2012).
- ¹⁹J. H. Song, T. Susaki, and H. Y. Hwang, *Adv. Mater.* **20**, 2528 (2008).
- ²⁰S. Valencia, Z. Konstantinovic, D. Schmitz, A. Gaupp, L. Balcells, and B. Martínez, *Phys. Rev. B* **84**, 024413 (2011).
- ²¹R. Bertacco, S. Brivio, M. Cantoni, A. Cattoni, D. Petti, M. Finazzi, F. Ciccacci, A. A. Sidorenko, M. Ghidini, G. Allodi, and R. De Renzi, *Appl. Phys. Lett.* **91**, 102506 (2007).
- ²²W. F. Egelhoff, P. J. Chen, R. D. McMichael, C. J. Powell, R. D. Deslattes, F. G. Serpa, and R. D. Gomez, *J. Appl. Phys.* **89**, 5209 (2001).
- ²³L. Brey, *Phys. Rev. B* **75**, 104423 (2007).