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2018

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Insights into the magnetic dead layer in La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films from temperature, magnetic field and thickness dependence of their magnetization

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Experimental investigations of the magnetic dead layer in 7.6 nm thick film of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) are reported. The *dc* magnetization (M) measurements for a sample cooled to $T = 5$ K in applied field $H = 0$ reveal the presence of negative remanent magnetization (NRM) in the M vs. H (magnetic field) measurements as well as in the M vs. T measurements in $H = 50$ Oe and 100 Oe. The M vs. T data in *ZFC* (zero-field-cooled) and *FC* (field-cooled) protocols are used to determine the blocking temperature T_B in different H. Isothermal hysteresis loops at different T are used to determine the temperature dependence of saturation magnetization (M_S), remanence (M_R) and coercivity H_C. The M_S vs. T data are fit to the Bloch law, M_S $(T) = M_0$ $(1 - BT$ $^{3/2})$, showing a good fit for $T < 100$ K and yielding the nearest-neighbor exchange constant $J/k_B \cong 18$ K. The variations of T_B vs. H and H_C vs. T are well described by the model often used for randomly oriented magnetic nanoparticles with magnetic domain diameter ≈ 9 nm present in the dead-layer of thickness $d = 1.4$ nm. Finally, the data available from literature on the thickness (D) variation of Curie temperature (T_C) and M_S of LSMO films grown under 200, 150, and 0.38 mTorr pressures of O$_2$ are analyzed in terms of the finite-size scaling, with M_S vs. D data fit to M_S $(D) = M_S(b)(1-d/D)$ yielding the dead layer thickness $d = 1.1$ nm, 1.4 nm and 2.4 nm respectively. Brief discussion on the significance of these results is presented. © *2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* https://doi.org/10.1063/1.5005913

Mixed valence manganese oxides with the formula RE$_{1-x}$A$_x$MnO$_3$ (RE = trivalent rare earth element; A = divalent alkaline earth element) have a wide range of electronic and magnetic phases depending on doping level and cation radii, making them useful in spintronic and magnetic memory devices.[1] Studies of thin films of La$_{1-x}$A$_x$MnO$_3$ showed above room temperature Curie temperature $T_C \sim 370$ K is achieved by doping Sr at the A-site with an optimum ratio of x $\sim$ 0.3,[2] making La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films good candidates for resistive switching memory devices, ferroelectric/ferromagnetic systems and heterostructures.[3–5] Studies on thin films of La$_{0.7}$Sr$_{0.3}$MnO$_3$ also showed that their magnetic properties are affected by film thickness and an inactive magnetic layer (dead layer) is present in thin films. Huijben *et al.* performed magnetic and transport measurements on LSMO thin films fabricated by pulsed laser deposition (PLD) with different thicknesses and reported that thin films remain ferromagnetic down to 3 unit cells.[6] Monsen *et al.* studied the thickness dependence of magnetic properties of LSMO thin films and determined a magnetic dead layer thickness d = 1.6 nm although the nature of magnetic state in the dead layer was not explored.[7]

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It has been suggested that the "dead layer" likely contains oxygen vacancies which disrupt exchange coupling and hence destroy long range order (LRO).[8]

Here we report detailed magnetic studies on a 7.6 nm thick film of $La_{0.7}Sr_{0.3}MnO_3$ on $SrTiO_3$ (100) prepared by pulsed laser deposition (PLD). Measurements of DC magnetization (M) were carried out in different applied magnetic fields (H) and temperatures (T) under the ZFC (zero-field-cooled) and FC (field-cooled) protocols to show that the blocking temperature (T_B) usually observed in magnetic nanoparticles (NPs) is also present in thin films. In addition, isothermal hysteresis loops were measured to determine the temperature dependence of saturation magnetization (M_S), coercivity (H_C) and remanence (M_R). M vs. T data show that in low H, negative remanent magnetization (NRM) exists below 100 K. Although the observation of NRM in LSMO film has been attributed to negative magnetic field trapped in superconducting magnet or uncompensated spins between ferromagnetic-ferroelectric layers,[9] a proper explanation for NRM is still lacking. To determine the parameters which affect the dead layer thickness d, data available from literature on the thickness (D) variation of T_C and M_S of LSMO films grown under three different O_2 pressures (200, 150 and 0.38 mTorr) are analyzed in terms of the finite size scaling, with M_S vs. D data fit to $M_S (D) = M_S(b)(1-d/D)$ yielding the dead layer thickness d = 1.1, 1.4 and 2.4 nm respectively (d = 1.4 nm for the 7.6 nm LSMO film). Details are given below.

The LSMO thin film with D = 7.6 nm was deposited on the TiO_2-terminated $SrTiO_3$ (100) substrate from the stoichiometric $La_{0.7}Sr_{0.3}MnO_3$ target by using a KrF excimer laser with the repetition rate of 5 Hz by PLD. During growth, the sample was heated in 750 °C and was exposed to 100 mTorr O_2 pressure and cooled down to room temperature at the rate of 15ºC/min in 250 mTorr O_2 pressure. The growth was monitored *in-situ* by reflection high energy electron diffraction (RHEED) to provide precise control of thickness down to unit cell scale. A physical property measurement system (PPMS) from Quantum Design with maximum H = 90 kOe was used to measure M vs. T from 5 K to 400 K with H applied in the plane of the film. The measured magnetic moment was scaled to the volume of the film (thickness ∗ area). Details of the procedures for magnetic measurements are given as a note in Ref. 10.

The plots of M vs. T for the ZFC and FC cases measured in H = 50, 100, 200, 500 Oe and 1 kOe are shown in Fig. 1. For the ZFC case, the sample was cooled to 5 K in H = 0 Oe and measuring H was then applied and M vs. T data taken up to 400 K. For the FC case, the sample is cooled to 5 K in non-zero H and M vs. T data taken similarly up to 400 K in the cooling H. Blocking temperature T_B defined here by the bifurcation of the M (FC) from the M (ZFC) data represents the temperature above which all spins are unblocked[11] and T_B decreases with increasing H. As expected, T_B is less than T_C, the latter defined by the inflexion point in the M vs. T data. Note the negative magnetization for the ZFC cases below 100 K for H = 50 Oe and 100 Oe. For H = 200 Oe and higher H, only positive values of M (ZFC) are observed. Any negative trapped residual magnetic field was practically eliminated by demagnetizing the magnet coil as described in Ref. 10. Note that the NRM has been reported in LSMO thin films.[9,12] and in some nanoparticle systems also.[13,14]

Temperature dependence of saturation magnetization (M_S), remanent magnetization (M_R) and coercivity (H_C) determined from the isothermal hysteresis loops for the ZFC sample are shown in Fig. 2. These data were corrected for the diamagnetic contribution of the substrate which was evident from the negative slope of the M vs. H plots at higher H (not shown here) where the ferromagnetic component of LSMO gets saturated. In the insets of Fig. 2, the hysteresis loop at 5 K and its low-field zoom are also shown. M_R is measured for H = 0 and M_S at H = 4 kOe. In Fig. 2, the initial M starts at negative values with the virgin loop requiring slightly larger field to switch sign. For H = 50 Oe, M (ZFC) is negative for $T < 100$ K becoming positive for $T > 100$ K. In the data of H_C vs. T in Fig. 2(c), H_C has dropped below 50 Oe. This explains why for $H < H_C$, the M (ZFC) is negative, leading to the result that $H < H_C$ leads to the observation of NRM for the ZFC sample.

For very thick films, M_S near 0 K was 583 (emu/cm^3) with $T_C \approx 350$ K.[7] For ferromagnetism $M_S = N_V \mu$ where N_V is the number of spins per unit volume each with magnetic moment μ. For $La_{0.7}Sr_{0.3}MnO_3 = La_{0.7}^{3+}Sr_{0.3}^{2+}Mn_{0.7}^{3+}Mn_{0.3}^{4+}O_3^{2-}$ with lattice constant a = 0.39 nm and calculated $N_V = 1.68 \times 10^{22}$/cm^3 yields μ = 3.74 μ$_B$ using M_S = 583 emu/cm^3. For Mn^{3+} (Mn^{4+}), the expected μ = 4 μ$_B$ (3 μ$_B$) using g = 2. This yields expected μ/μ_B = [(0.7)(4)+(0.3)(3)] = 3.7 in excellent
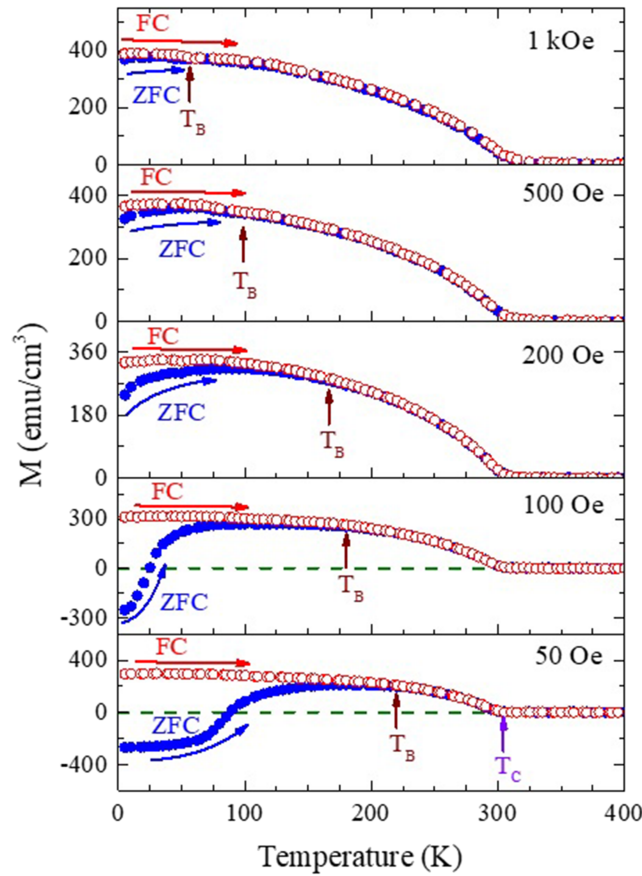
FIG. 1. Magnetization vs. temperature data for the 7.6 nm LSMO/STO sample measured with H = 50, 100, 200, 500 Oe and 1 kOe. Arrows mark the bifurcation temperature T_B separating the M (FC) data (open red circles) from the M (ZFC) data (closed blue circles). T_C is the Curie temperature.

agreement with the measured μ = 3.74 μ_B for thick films. For the 7.6 nm thick film, the measured M_S = 476 (emu/cm^3) is lower than M_S = 583 emu/cm^3 because of the dead layer problem discussed later. For M_S = 476 (emu/cm^3), μ = 3.05 μ_B is obtained which gives S = 3/2 for g =2 used in the calculations below.

The decrease of M_S with increasing T shown in Fig. 2(a) for the 7.6 nm film is due to the excitation of spin waves (magnons). This temperature dependence of M_S is fit to the Bloch's $T^{3/2}$ law given by[15]

$$\Delta M_S/M_S(0) = (0.0597/QS)(k_B T/2JS)^{3/2}. \tag{1}$$

Here Q = 1, 2, or 4 for a sc, bcc or fcc structures and $\Delta M_S = M_S(0) - M_S(T)$. Bloch's law is derived using the Heisenberg Hamiltonian: $H = -2J \sum_{i=1}^{N} S_i.S_{i+1}$ where J is the exchange constant, and S_i is the spin of atom "i". For LSMO, there is only one magnetic ion per unit cell and so Q = 1. The lines in Fig. 2(a) are fits to Eq. (1) using S = 3/2 and exchange constant J/k_B = 18 K and 20 K. Thus the temperature variation of M_S can be explained by the excitation of magnons represented by the Bloch's $T^{3/2}$ law reasonably well. Another estimate of J is determined from T_C using molecular field theory, yielding $J/k_B = 3T_C/2ZS(S+1)$. With Z = 6 as the number of exchange-coupled nearest neighbors each with spin S =3/2 and T_C = 305 K for the 7.6 nm LSMO film gives J/k_B = 20 K close to J/k_B = 18 K determined above.

The temperature variation of M_R and H_C in Fig. 2 shows that both become zero near 240 K coinciding with measured $T_B \approx$ 230 K in H = 50 Oe. In Fig. 3(a), the dependence of T_B on H is seen to fit very well to $T_B (H) = T_B(0)[1-(H/H_0)^2]$ observed in NPs.[16] It is proposed that the observation of a bifurcation between ZFC and FC is due to nanoclusters of spins in the dead layer of thickness
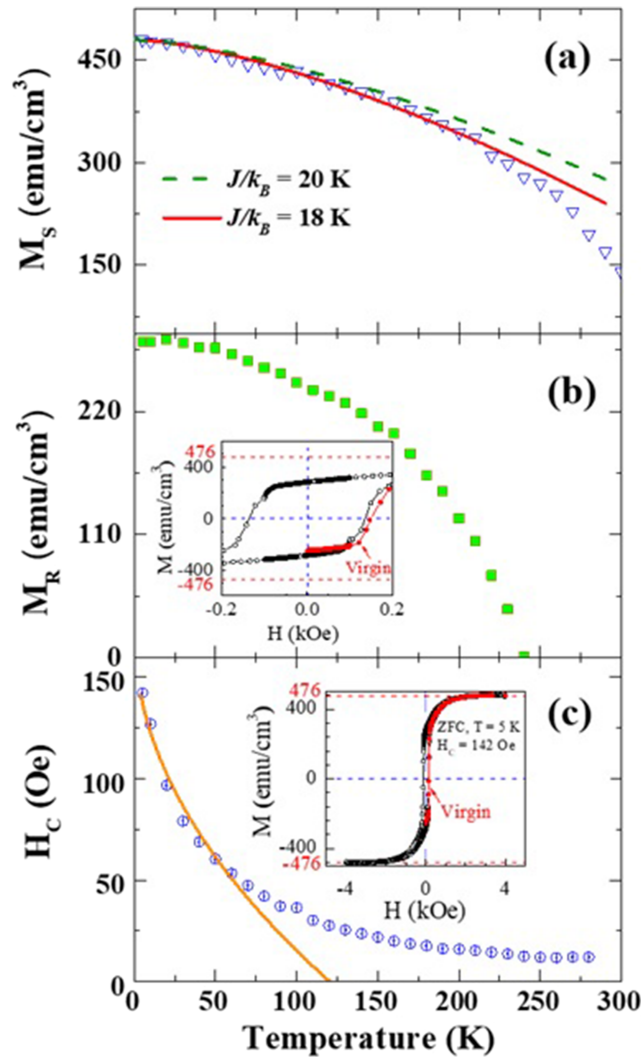
FIG. 2. Variation of M_S, M_R and H_C vs. temperature. The solid and dashed lines in (a) are fits to Eq. (1). In the inset of (b) and (c), hysteresis loop for the low field range and up to 4 kOe respectively are shown. In (c) the solid line is fit to H_C (T) = H_{C0} $[1 - (T/T_B)^{1/2}]$.

d = 1.4 nm (determined later) in the 7.6 nm film. If D_0 is the average diameter of the nanocluster, then its volume $V \approx D_0^2 d$. For non-interacting NPs, $k_B T_B = KV/25$ yielding $V = 25\, k_B T_B/K$ where K is the anisotropy constant of the film.[17] Also the anisotropy constant K and coercivity H_C are related by the Eq. $H_C \approx K/M_S$. Using $M_S = 476$ emu/cm^3 and $H_C \approx 150$ Oe measured at 5K, yields $K = 7.2 \times 10^4$ ergs/cm^3. Using this value of K and $T_B = 230$ K yields $V = D_0^2 d = 1.1 \times 10^{-17}$ cm^3 leading to $D_0 \approx 9$ nm as the diameter of the spin cluster for $d = 1.4$ nm.

For randomly oriented and non-interacting NPs, H_C (T) vs. T varies as H_C $(T) = H_{C0}$ $[1 - (T/T_B)^{1/2}]$.[18,19] In Fig. 2(c), the fit of the data to this Eq. for lower T appears to be valid but the fit for higher T fails and extrapolated $T_B = 120$ K $< T_B = 230$ K with $H = 50$ Oe. This difference is likely due to the fact that to measure H_C, $H = 4$ kOe was used and T_B is strongly dependent on H.

To understand the issue of the 'dead layer" and its role in the magnetic properties of thin films, variation of T_C and M_S with respect to film thickness D are modeled by using the available data from literature on thin films prepared in different O_2 deposition pressures which is shown to significantly affect the measured properties. Experiments show that T_C and M_S decrease with decrease in thickness of the films which is similar to the observations reported in magnetic NPs.[6,20] We model the variation of M_S vs. thickness D of thin film using the derived Eq.: M_S $(D) = M_S(b)$ $(1-d/D)$,
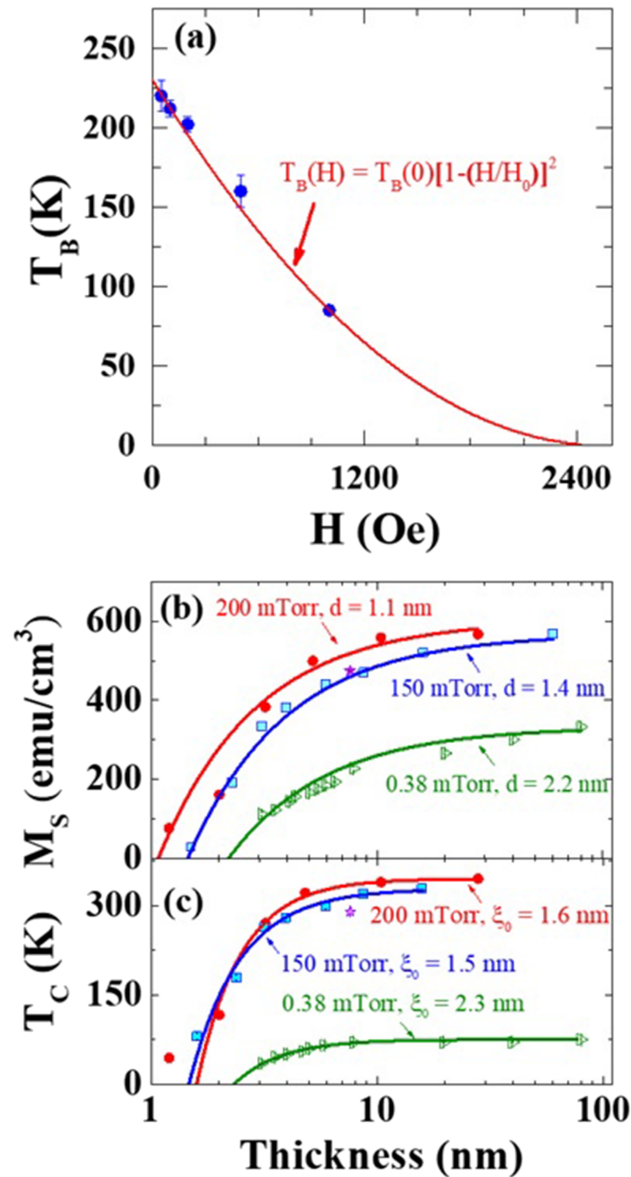
FIG. 3. (a). Variation of T_B with applied field H; (b) Variation of the Ms and T_C with thickness D of the LSMO films. Different symbols represent data from different groups as follows: solid blue rectangle,[6] solid red circle,[20] open green diamond.[7] The solid lines are fits to $M_S (d) = M_S(b) (1-d/D)$ in (b) and to Eq. (2) in (c) with the listed parameters.

where d is the thickness of dead layer which is not contributing to M_S, and $M_S(b)$ is the saturation magnetization for bulk sample. To check the validity of this model, we show in Fig. 3(a) the plot of M_S vs. D from three sets of films grown in 200, 150 and 0.38 mTorr O_2 pressures with the solid lines fits to $M_S (D) = M_S(b) (1-d/D)$ yielding d =1.1, 1.4 and 2.4 nm for 200, 150 and 0.38 mTorr O_2 pressures respectively. For these data taken from literature,[6,7,21] each point was accurately determined using the internet available software 'WebPlotDigitizer' and the data for the 7.6 nm film is shown by the star symbol in Fig. 3. The data fit the model well, showing that with decrease in O_2 pressure, M_S is lowered and d increases. Magnetic properties of manganites are governed by the double-exchange interaction between d-orbitals of magnetic Mn^{3+} and Mn^{4+} ions with charge transfer from Mn^{3+} to Mn^{4+} ions through oxygen atoms. Low O_2 pressure increases oxygen vacancies, resulting in breakdown of the exchange mechanism and increased spin disorder which in turn decreases M_S and T_C.

The variation of T_C with film thickness D of LSMO films is modeled by the finite-size scaling relation:

$$T_C(D) = T_C(\infty)\left[1 - (\xi_0/D)^\lambda\right] \qquad (2)$$

where $T_C(D)$ and $T_C(\infty)$ are respectively the Curie temperatures for a film with thickness D and very thick films, λ is the shift exponent and ξ_0 is characteristic microscopic correlation length.[22] The fit of the data to Eq. (2) are shown in Fig. 3(c) for the films grown in different O_2 pressures with the parameters obtained from the fit listed in the figure. The value of λ depends on the theoretical model, $\lambda = 2$ is obtained from Monte-Carlo simulation.[23]

In conclusion, using the analysis of the results from magnetic measurements, it is shown that the magnetic dead layer of thickness $d = 1.4$ nm in the 7. 6 nm LSMO film consists of clusters of ordered spins of about 9 nm diameter with nearest neighbor exchange coupling $J/k_B \cong 18$ K among the spins. Also reported here is the observation of NRM in ZFC samples with measuring $H < H_C$. Additional studies on the origin of NRM are in progress and these results will be reported soon.

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[10] For each measurement, the magnet coil was first demagnetized at ambient since without demagnetizing the coil, the residual $H \sim 25$ Oe is present but after demagnetizing the coil, the residual H is reduced to < 2 Oe. Next the sample centering was done at ambient in $H = 1$ kOe, followed by raising the temperature to 360 K (which is above T_C) to remove any remanence in the sample. The sample was then cooled to 5 K in zero applied H. After waiting for 15 minutes at 5 K to ensure temperature stability, a measuring H was then applied. For measuring M vs. T starting from 5 K, a sequence file is created for the temperatures at which M is to be measured, typically in 2-degree steps. The temperature sweep rate was 5 K/min but temperature is stabilized at each measuring temperature for about 15 seconds during which the data of magnetic moment at that temperature is acquired. The system then automatically goes to the next measuring temperature and the procedure is repeated. The isothermal data of M vs. H were acquired using similar procedures. The lateral dimensions of the film and substrate are: 4.98 mm $\times$ 5.81mm.

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