

# Phase coexistence and magnetic anisotropy in polycrystalline and nanocrystalline $\text{LaMnO}_{3+\delta}$

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We report on the phase coexistence and magnetic anisotropy in polycrystalline (bulk) and nanocrystalline ( $\sim 15$  nm)  $\text{LaMnO}_{3+\delta}$  materials, which were prepared by solid state reaction and sol-gel methods, respectively. In addition to standard magnetization measurements, radio-frequency transverse susceptibility (TS) based on a very sensitive, self-resonant tunnel diode oscillator method was used to probe magnetic anisotropy and switching fields in the samples. The results revealed a coexistence of the ferromagnetic (FM) and antiferromagnetic (AFM) phases in both samples. For the bulk sample, the AFM phase significantly changed in volume fraction at  $\sim 30$  K and completely vanished around 120 K. Size reduction to the nanometer scale ( $\sim 15$  nm) significantly suppressed the AFM phase while inducing surface spin disorder in the material. The large magnetic anisotropies were probed by TS experiments in both samples. Our studies showed that the magnetic properties of bulk  $\text{LaMnO}_{3+\delta}$  were strongly modified by size reduction. © 2011 American Institute of Physics. [doi:10.1063/1.3551734]

## I. INTRODUCTION

Perovskite materials of  $\text{LaMnO}_{3+\delta}$  have been an area of intense research due to their interesting magnetotransport properties<sup>1,2</sup> and applications in high-temperature solid-oxide fuel cells.<sup>3,4</sup> It was shown that depending on the synthesis procedure and annealing temperature, cationic vacancies could be introduced in the stoichiometric compound that originated from occurrence of  $\text{Mn}^{4+}$  cations.<sup>4,5</sup> The oxygen stoichiometry of the sample depended on the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  concentration, which strongly affected the magnetic ordering transition temperatures,<sup>6</sup> crystal structure,<sup>7</sup> and exchange energy scales<sup>8</sup> within the material. While the magnetic properties of bulk  $\text{LaMnO}_{3+\delta}$  with  $\delta$  variation were reported in several previous works,<sup>1,6,9,10</sup> no study has been done on the effect of size reduction on the phase coexistence and magnetic anisotropy in the material.

We present here a comparative study of the static and dynamic magnetic properties of bulk ( $\delta = 0.09$ ) and nanocrystalline ( $\delta = 0.12$ )  $\text{LaMnO}_{3+\delta}$ . We show the coexistence of the FM and AFM phases in both samples. Size reduction to the nanometer scale ( $\sim 15$  nm) was found to change the structure and significantly suppress the AFM phase, while inducing surface spin disorder in the material. The magnetic anisotropy and its temperature and magnetic field dependence in the bulk and nanocrystalline samples were probed by transverse susceptibility (TS) experiments.

Bulk  $\text{LaMnO}_{3+\delta}$  was prepared by using solid state synthesis method. The high purity (Sigma Aldrich)  $\text{La}_2\text{O}_3$  and  $\text{MnCO}_3$  were used as precursor material for  $\text{LaMnO}_3$ .  $\text{La}_2\text{O}_3$

was preheated at  $800^\circ\text{C}$  for 3 h, and  $\text{MnCO}_3$  was preheated to  $200^\circ\text{C}$  for 2 h. After mixing and grinding, it was calcined in air at  $1200^\circ\text{C}$  for 12 h; final heat treatment was done at  $1300^\circ\text{C}$  for 12 h and then it was quenched. The nanocrystalline sample (henceforth the nano sample) was synthesized using a modified sol-gel route, where high purity La-acetate and Mn-acetate (procured from Sigma Aldrich) were used. The precursor was dissolved in 1:1 stoichiometric proportion of acetic acid and water. An appropriate amount of ethylene glycol (molecular weight =  $62.07$  g/mol) was added and heated until the gel was formed. It was then dried overnight at  $150^\circ\text{C}$ . Pyrolysis was done at  $350$  and  $450^\circ\text{C}$ , followed by calcination at a higher temperature of  $650^\circ\text{C}$  to obtain the desired chemical phase. The phase formation and purity of the bulk and nano samples was confirmed by x-ray diffraction (XRD).

Magnetic measurements were performed using a commercial physical property measurement system (PPMS) from Quantum Design. The magnetic anisotropy and switching fields in the samples were probed by TS using a sensitive, self resonant tunnel diode oscillating (TDO) technique<sup>11</sup> with a resonant frequency of  $\sim 20$  MHz. The sample was placed in the inductance coil of the tank circuit integrated into the PPMS. The TS measurement for a given temperature was performed by monitoring the change in the resonant frequency of the circuit as the dc field was swept from positive saturation to negative saturation and then back to positive. Because the change in frequency ( $f$ ) of the resonant circuit is a direct consequence of the change in inductance as the sample is magnetized, the quantity  $\Delta f$  is directly proportional to  $\Delta\chi_T$ . In this study, we considered the quantity,  $\Delta\chi_T/\chi_T$  (%) =  $\{[\chi_T(H) - \chi_{\text{sat}}]/\chi_{\text{sat}}\} \times 100$ , where  $\chi_{\text{sat}}$  is the transverse susceptibility at a saturation field.

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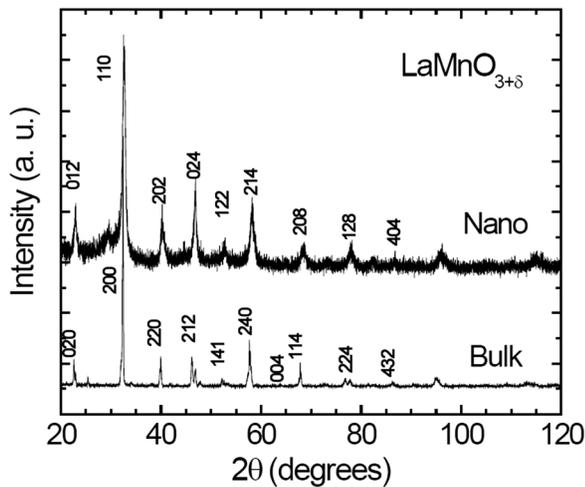


FIG. 1. XRD patterns of the  $\text{LaMnO}_{3+\delta}$  bulk and nanocrystalline samples.

Figure 1 shows the XRD patterns of the bulk and nano samples. While the bulk sample was found to exhibit an orthorhombic structure with the lattice parameters ( $a = 5.5953 \text{ \AA}$ ,  $b = 7.7488 \text{ \AA}$ ,  $c = 5.5473 \text{ \AA}$ ), the nano sample possessed a rhombohedral structure with the lattice parameters ( $a = 5.4943 \text{ \AA}$ ,  $b = 5.4943 \text{ \AA}$ ,  $c = 13.317 \text{ \AA}$ ). The average particle size of the nano sample was determined to be 15 nm by using transmission electron microscopy. The structural change upon size reduction would strongly modify the magnetic properties of the material as discussed in the following text.

Figure 2 shows the temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetization taken in 200 Oe for the bulk and nano samples. The inset of Fig. 2 shows the  $M(H)$  loops taken at 10 K for these samples. The  $M(T)$  data indicated that the bulk sample underwent an antiferromagnetic transition at  $T_N \sim 110 \text{ K}$ , which was consistent with the neutron diffraction (ND) data (not shown) that indicated that the intensity of the AFM peak decreased with increasing temperature and vanished at  $\sim 116 \text{ K}$ . The minor peaks due to FM order were also detected in the ND spectra. These results evidenced the coexistence of both AFM and FM phases below  $T_N$ . The phase coexistence below 110 K was also reported in bulk  $\text{LaMnO}_{3+\delta}$  with  $\delta = 0.05$  by Palomares *et al.*<sup>6</sup> In addition to this transition,

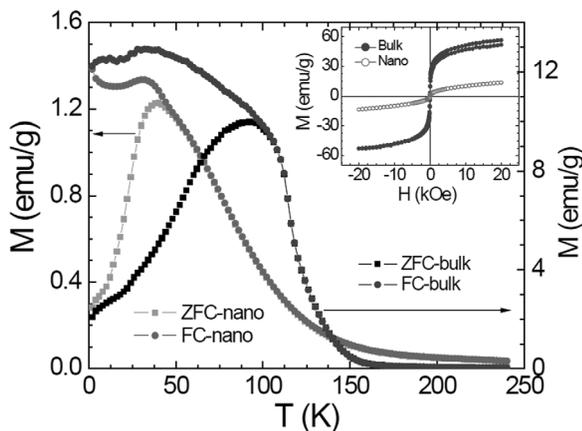


FIG. 2. (Color online) Temperature dependence of magnetization taken in a field of 200 Oe in the ZFC-FC regimes for the bulk and nanocrystalline samples. The inset shows the  $M(H)$  loops for these samples.

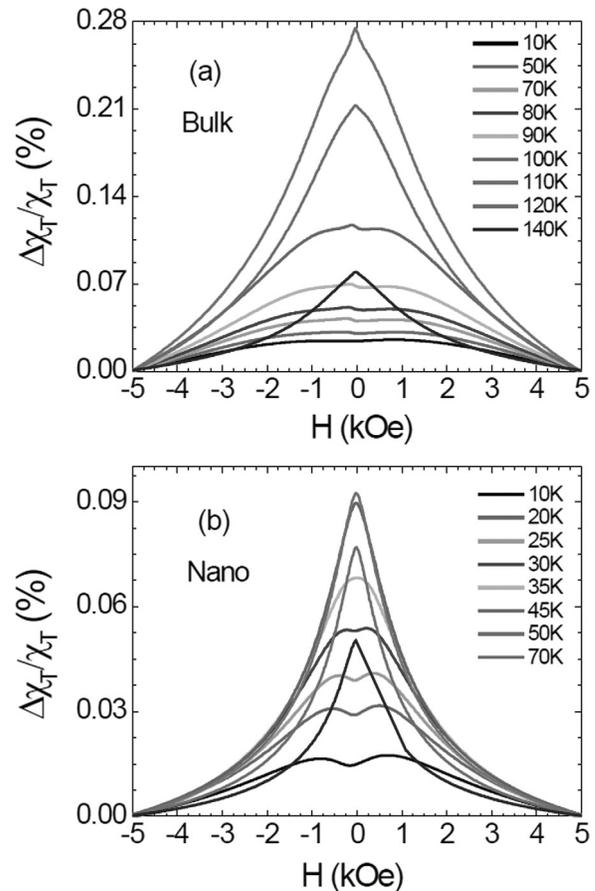


FIG. 3. (Color online) TS spectra for unipolar scans from positive (+5 kOe) to negative (−5 kOe) fields for the bulk and nanocrystalline samples.

we also observed a slight decrease in the FC magnetization at 30 K, due to the increase in volume fraction of the AFM phase as probed by TS experiments in the preceding text. Size reduction to the nanometer scale (15 nm) shifted the transition temperature to  $\sim 30 \text{ K}$ . A sharp increase in the FC magnetization observed for this sample below  $\sim 15 \text{ K}$  could be attributed to freezing of surface spins as a consequence of size reduction. The inset of Fig. 2 shows that the saturation magnetization ( $M_S$ ) taken at 10 K (56.6 emu/g) of the bulk sample was about three times larger than that of the nano sample (13.5 emu/g). The decrease of  $M_S$  in the nano sample was likely attributed to the presence of surface spin disorder. Noticeably, the  $M(H)$  loop for the bulk sample did not close when the field was swept back from negative to positive saturation at 2 T. A similar feature was reported on a polycrystalline  $\text{Pr}_{1/3}\text{Ca}_{2/3}\text{MnO}_3$  and attributed to the coexistence of the FM and AFM phases.<sup>12</sup> Noticeably this feature was not pronounced in the nano sample, which could be associated with the strong suppression of the AFM peak in the ND spectra for this sample. Overall, our magnetic and neutron diffraction data consistently indicated the coexistence of the FM and AFM phases in the bulk and nano samples, and size reduction to the nanometer scale ( $\sim 15 \text{ nm}$ ) significantly suppressed the AFM phase while inducing surface spin disorder in the material. Due to the excess oxygen ( $\delta$ ),  $\text{Mn}^{4+}$  ions were introduced into the material, leading to a formation of  $\text{Mn}^{4+}$ - $\text{Mn}^{3+}$  ferromagnetic pairs (formed ferromagnetic

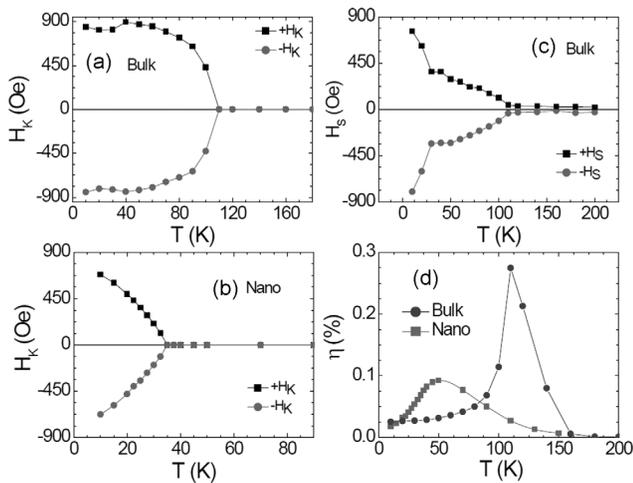


FIG. 4. (Color online) Temperature dependence of the magnetic anisotropy field ( $H_K$ ) for the bulk sample [Fig. 3(a)] and for the nanocrystalline sample (b), the magnetic switching field ( $H_S$ ) for the bulk sample (c), and the height of the TS peak ( $\eta$ ) for both samples.

clusters) embedded in a  $Mn^{3+}$ - $Mn^{3+}$  antiferromagnetic matrix. This could explain the coexistence of both AFM and FM phases in the present samples.

To probe the magnetic anisotropy and switching fields in the bulk and nano LaMnO<sub>3+δ</sub> samples, we used the TS technique that has been validated by us to study the anisotropic magnetic properties of thin films<sup>13</sup> and nanoparticle systems.<sup>14</sup> Aharoni *et al.*<sup>15</sup> theorized that the TS for a Stoner–Wohlfarth particle with its hard magnetic axis aligned with the dc field should yield peaks at the anisotropy fields ( $\pm H_K$ ) and switching field ( $H_S$ ) as the dc field is swept from positive to negative saturation. However, our TS experiments have revealed that for magnetic nanoparticle systems with size distribution, the switching peak is often merged with one of the anisotropy peaks.<sup>14</sup> In the present study, the TS data were collected over a temperature range 10 K <  $T$  < 300 K for the bulk and nano samples. For clarity, we present in Figs. 3(a) and 3(b) the TS spectra with unipolar field sweeps from positive (+5 kOe) to negative (-5 kOe) fields for selected temperatures for both samples. Clearly, the TS spectra exhibited a two-peak structure at low temperatures, which merged into a single central peak at high temperatures. The height of the TS peak [ $\eta = (\Delta\chi_T/\chi_T)_{\max}$  (%)] also varied strongly with temperature around the transition temperature for these samples.

To better capture these features, we plot in Figs. 4(a)–4(d) the temperature dependence of  $H_K$ ,  $H_S$ , and  $\eta$  for both samples. Note that the peak corresponding to  $H_S$  was detectable in the bulk sample but not in the case of the nano sample because it merged with the anisotropy peak (on the negative side,  $-H_K$ ). Therefore we only display in Fig. 4 the temperature dependence of  $H_S$  for the bulk sample. As one can see clearly from Figs. 4(a) and 4(b), the  $H_K$  increased with decreasing temperature just below the transition temperatures 110 and 30 K for the bulk and nano samples, respectively. Larger values of  $H_K$  were obtained for the bulk sample as compared to the nano sample. For the bulk sample, we also observed a slight decrease in  $H_K$  at 30 K [Fig. 4(a)], which coincided with the increase in  $H_S$  at this temperature

[Fig. 4(c)]. This was likely associated with the decrease in the FC magnetization as we noted in the preceding text in Fig. 2. These results suggested a phase re-distribution occurring around 30 K, at which the AFM phase significantly changed in volume fraction. We also note that the  $H_S$  reached zero as the temperature increased above 120 K [Fig. 4(c)]. This indicated that the AFM phase disappeared as  $T > 120$  K, consistent with the neutron diffraction data. For the nano sample the nearly linear increase of  $H_K$  with temperature below 30 K was noted [Fig. 4(b)], which could be attributed to the presence of surface spin disorder. We plotted the change in height ( $\eta$ ) of TS peaks with temperature [Fig. 4(d)], and it shows that the  $\eta$  reached a maximum at 110 and 30 K for the bulk and nano samples, respectively. However, the  $\eta$  of the nano sample was lower than that of the bulk, which was consistent with the magnitude of magnetization (Fig. 2).

In summary, the static and dynamic magnetic properties of LaMnO<sub>3+δ</sub> bulk and nanocrystalline materials were studied. The ferromagnetic and antiferromagnetic phases coexisted in these samples. For the bulk sample, the AFM phase significantly changed in volume fraction at  $\sim 30$  K and completely vanished around 120 K. Size reduction to the nanometer scale ( $\sim 15$  nm) changed the structure and significantly suppressed the antiferromagnetism while inducing surface spin disorder in the material. Both the bulk and nanocrystalline samples exhibited large magnetic anisotropy, which increased with decreasing temperature below their transition temperatures.

## ACKNOWLEDGMENTS

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