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Strain modulated magnetization and colossal resistivity of epitaxial $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ film on BaTiO_3 substrate

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A sharp drop in resistance and a magnetization anomaly have been observed in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ film in zero magnetic field at the BaTiO_3 substrate structural phase transition temperature, due to the substrate clamping/strain effect, which is confirmed by Raman scattering. However, the anomalies for both resistance and magnetization were eliminated by a strong external magnetic field. These phenomena indicate that strain can cause colossal resistance and a change in magnetization which resembles the magnetic field effect. The interplay of the external forces (strain and magnetic field) is a good demonstration of the strong coupling between spin and lattice in colossal magnetoresistance materials. © 2011 American Institute of Physics. [doi:10.1063/1.3633101]

The colossal magnetoresistance (CMR) manganite perovskites have attracted considerable attention due to their potential applications and fascinating physical properties, such as phase separation, charge ordering, and the CMR effect. A strong interplay among the degrees of freedom, involving charge, lattice, spin, and orbital ordering, has been found in CMR materials.^{1–4} Therefore, for a film-on-substrate structure, the substrate-induced lattice strain can modify the physical properties of the CMR manganite through modification of the Mn–O–Mn bond lengths and angles, and thus modify the strength of double exchange (DE) and the Jahn-Teller (JT) lattice-electron coupling.^{5–12} A number of experiments have shown the existence of such strain effects, for example, strain modified magnetisation and resistivity under static or dynamic adjustable strain.^{13–18} It is well known that magnetic field can cause similar modification in the magnetization and the resistivity of CMR materials. The modification caused by magnetic field should resemble what is caused by strain, if the modifications caused by magnetic field and strain can be sourced to the interplay of spin, charge, and lattice. Although this viewpoint has been widely accepted, the experimental evidence is currently unavailable, although highly desirable.

In this letter, a slice of (001) cut BaTiO_3 (BTO) was used as the substrate for the epitaxial growth of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ (LCMO) CMR thin film. The strain state of LCMO film epitaxially grown on a BTO substrate is subject to large changes at the phase transition temperatures of BTO, especially at the Rhombedral-Orthorombic (R-O) transition of BTO (~ 190 K). Such a change in the strain state will introduce a strong change in the lattice distortion. It is speculated that magnetic and transport properties of the films will be significantly modified by such a dynamic structural change. In combination with or comparison to the effect caused by magnetic field simultaneously applied on the film, experimental evidence showing the similarity of the effects of magnetic field and strain modulation on physical properties of CMR materials can thus be provided.

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The thin film samples in this work were deposited at 600°C in a reduced dynamic flowing oxygen atmosphere of 200 mTorr, using a pulsed laser deposition (PLD) system. The thickness of the obtained thin film was around 100 nm, which is within the strain relaxation thickness of epitaxially grown film. The structure of the film was determined by using $\text{Cu K}\alpha$ radiation on a JEOL 3500 x-ray diffraction (XRD) machine. Raman scattering was carried out to examine the structural change in the LCMO film at the BTO substrate phase transition temperature, using a Micro-Raman system with a 514.5 nm laser, as Raman spectra have ultra-high spatial resolution, which means that a shift of 1 cm^{-1} in frequency quantitatively measures a change of 0.0003 nm in bond length.¹⁹ The magnetic and transport properties of the sample were examined on a Quantum Design 14 T physical properties measurement system (PPMS).

Figure 1 shows the XRD pattern of a $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ thin film on a BaTiO_3 substrate fabricated by the PLD method. Only the (001) and (002) peaks of LCMO were observed near the BTO (100)/(001) and (200)/(002) diffraction peaks, indicating that LCMO film shows a strong epitaxial growth habit on a BTO substrate. The expected 90° domain structure in the BTO substrate is also demonstrated by the presence of (002) and (200) diffraction peaks in the XRD pattern. The lattice parameters of the BTO substrate

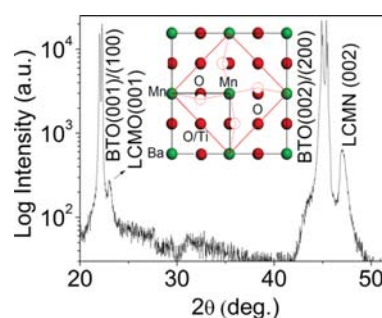


FIG. 1. (Color online) X-ray diffraction pattern of the LCMO/BTO sample measured at room temperature. Inset is the crystal structure of the LCMO film on BTO substrate, a top view of one LCMO cell above a 2×2 BTO supercell.

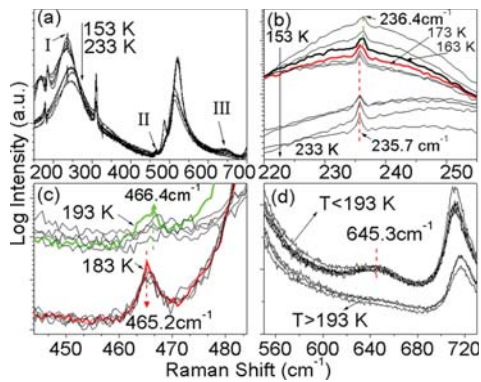


FIG. 2. (Color online) (a) Raman spectra of the LCMO/BTO film from 153 K to 233 K. (b) Magnified view of peak I. (c) Magnified view of peak II. (d) Magnified view of peak III.

are calculated as $a = 3.955 \text{ \AA}$ and $c = 4.001 \text{ \AA}$, based on the above XRD pattern, while the pseudocubic lattice parameter of LCMO film is $c = 3.83 \text{ \AA}$. In comparison to the standard value, $c = 3.86 \text{ \AA}$, of bulk LCMO, this result shows that the LCMO film is compressed in the out-of-plane direction with large compressive strain.

In Figure 2(a), the Raman spectra of the film are dominated by the strong Raman scattering peaks from the substrate, and only a few weak peaks from LCMO can be observed due to its pseudocubic symmetry. Three peaks are located at around 235, 465, and 645 cm^{-1} , which are ascribed to the y-rotation, bending, and stretching modes of Mn–O octahedra, respectively.²⁰ The two high frequency phonons (bending and stretching modes) are associated with modifications of the Mn–O bond, while the low frequency one is assigned to rigid rotations of the octahedra. Figure 2(b) shows that there is a peak shift of 0.8 cm^{-1} to higher frequency of the y-rotation mode between 163 K and 173 K. This shift takes place at a temperature lower than the temperature where the substrate phase transition occurs, and thus, it is difficult to directly attribute this shift to the substrate phase transition. In Figure 2(c), the bending mode shows a shift of 1.2 cm^{-1} to the lower frequency side at temperatures lower than 193 K, with a simultaneous increase in peak intensity. In Figure 2(d), the Raman scattering peak from the stretching mode disappears at temperatures above 193 K. The temperatures for the shifting of the bending mode and the vanishing of the stretching mode coincide with the temperature for the substrate structural phase transition, which indicates that the structure of the LCMO film is modulated by the BTO R-O phase transition.

Figure 3(a) shows that a paramagnetic to ferromagnetic transition starts at 244 K for the sample in the 100 Oe DC field, while the transition temperature shifts to 277 K and 296 K when higher fields of 2000 Oe and 1 T are applied, respectively (M-T curve). Distinct anomalies with concomitant thermal hysteresis are observed on both the field cooled and the zero-field cooled (FC-ZFC) magnetization curves between 188 K and 200 K, measured at 100 Oe, where the BTO R-O phase transition and LCMO Raman scattering abnormal occur. Similar magnetization anomalies were also observed for the FC magnetization curve at an applied magnetic field of 2000 Oe, but with much reduced magnitude. However, such

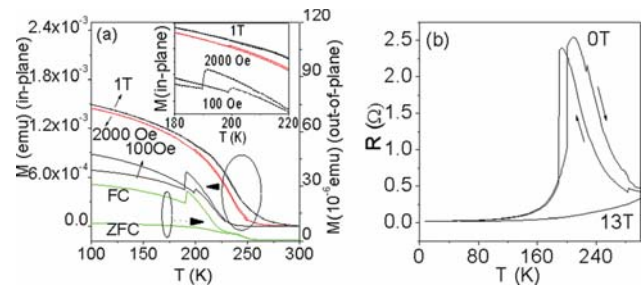


FIG. 3. (Color online) (a) Field cooled and zero-field cooled in-plane and out-of-plane magnetization curves of the LCMO/BTO film measured under different magnetic fields; inset is an enlargement of the indicated temperature range. (b) Temperature dependence of resistance of the LCMO/BTO film measured under 0 T and 13 T.

anomalies were not clearly observed for the magnetization curve measured under the highest magnetic field of 1 T, which means that a strong external magnetic field can suppress the jump in magnetization. This result demonstrates that we are able to modulate the magnetic response of LCMO via strain, but this can only happen at low magnetic field. The out-of-plane magnetization FC and ZFC curves of the same sample at a magnetic field of 100 Oe show a magnetic moment of two orders of magnitude smaller than for the in-plane case, indicating strong magnetic anisotropy.

Similar to the M-T curves, thermal hysteresis is also observed in the resistivity vs. temperature measurements (R-T curves), as evidenced by the resistance peak positions at 208 K and 193 K for heating and cooling measurements, respectively (shown in Fig. 3(b)). In addition, an abrupt decrease in the resistance jump was observed for both the cooling and the heating processes in R-T curves. The decrease in the magnitude of the jump in the resistance between 0 T and 13 T is $(2.36 - 0.5)/2.36 = 78.8\%$. The temperatures for the occurrence of the abrupt decrease in resistance are at the same temperatures as for the occurrence of magnetization anomalies, the BTO R-O phase transition, and the abnormal LCMO Raman scattering peak. This abrupt change indicates that modulation of the strain in LCMO film by substrate R-O structural transformation modifies the transport behaviour as well as the magnetization. In addition, both the magnitude and sign of the resistivity changes remain constant through many thermal cycles, indicating that the structural effects are elastic and reversible. Since cracks can be easily formed in BaTiO_3 , one cannot completely eliminate the possibility of substrate induced cracking in the film. Cracking will cause an irreversible increase in the resistivity. However, the observed decrease in the resistivity in this study should not have any relationship to cracks.

In CMR materials, the semiconductor-metallic state transition takes place simultaneously with the paramagnetic-ferromagnetic (PM-FM) ordering. The relationship between conductivity and magnetic ordering at and below the transition temperature is explained by a double exchange mechanism and Jahn-Teller electron-lattice coupling, for which the Mn–O–Mn bond length and angle are the key factors.^{21–23} Thermal cycling of the BTO crystal during the temperature dependent measurements leads to the formation of different types of crystal domains. These BTO domains give rise to

two different strains in a magnetic film and two different modulations of strain at the BTO phase transition. The lattice parameters of BTO change from 4.013 Å (*a* and *b* axes) and 3.99 Å (*c* axis) to 4.001 Å, with a deviation of 90° to 89.85° for the *a*/*b* angle at the O-R phase transition. A change in the in-plane lattice parameters will change the Mn–O–Mn bond length and bond angle, which is evidenced by Raman peak shifting, similar to the effect caused by Jahn–Teller distortion and will eventually change the resistance of the film, according to the DE mechanism. However, the high magnetic field of 13 T was found to eliminate the observed sharp resistance jumping in R-T measurements, and the resistance in high magnetic field below the R-O phase transition temperature is much smaller than the value measured without magnetic field. This means that magnetic field can produce similar structural distortion effects to what is produced in LCMO film by strain from substrate phase transitions. Such an effect produced by magnetic field, however, is much stronger than the effect caused by a substrate phase transition. It has been recognized that CMR materials experience a significant magnetostriction effect, with the magnitude of volume change up to 0.1% at the Curie temperature, T_C , due to strong electron-lattice interaction or Jahn-Teller distortion when the 3d e_g electrons start to delocalize at temperatures approaching T_C from the high temperature side.^{24–26} Such a delocalization of 3d electrons favours DE, and an insulator to metal-like transition takes place. The changing lattice distortion in LCMO film at the BTO phase transition temperature will affect the status of the e_g electrons due to strong electron-phonon interaction and accelerates the process of delocalization of e_g electrons, eventually leading to a sharp decrease in resistance. Therefore, the observed anomaly in R-T measurements at the R-O transition indicates the existence of strong electron-lattice interaction in CMR materials and strong effects of the interaction on the physical properties. However, the magnitude of the change in the lattice distortion due to the substrate is less than that caused by the magnetostriction effect in LCMO film when a strong magnetic field is applied. Therefore, high magnetic field can easily eliminate the observed resistance jumping in zero magnetic field. Similarly, the large structural distortion in high magnetic field caused by strong electron-lattice interaction can mask the external disturbance, and thus, the magnetic moment anomaly is destroyed by high magnetic field. It has proposed that the changing of the magnetic anisotropy and magnetic domain is the cause for the modification of the magnetization at BTO substrate structure phase transition in other kinds of magnetic film (non-CMR film).^{27,28} However, for those films and such a cause, magnetic field can kill the modification of magnetization but not the resistivity, which is different from what has been observed in this report. Therefore, at least the modification of the magnetic anisotropy and the magnetic domain of CMR film at BTO phase transition is not the only reason for the observation in this report.

In summary, in a LCMO film grown on a BTO substrate, anomalies were observed on both M-T and R-T curves at the BTO R-O phase transition. Both the anomalies in the magnetization and the resistance drop can be eliminated by a strong magnetic field. All these phenomena indicate that colossal resistance change in CMR material at temperatures around the PM-FM transition can be produced solely by strain as well as by magnetic field. In addition, structural distortion in CMR material caused by high magnetic field is much stronger in magnitude than structural distortion produced by the substrate clamping effect and phase transition. This unique observation reveals the interplay between lattice and spin in CMR materials under external forces (strain and magnetic field).

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