FAST TRACK COMMUNICATION

Large anisotropy in colossal magnetoresistance of charge orbital ordered epitaxial $Sm_{0.5}Ca_{0.5}MnO_3$ films

Y Z Chen[1,2]**, J R Sun**[1]**, J L Zhao**[1]**, J Wang**[1]**, B G Shen**[1] **and N Pryds**[2]

[1] State Key Laboratory of Magnetism, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China
[2] Fuel cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Denmark

E-mail: yunc@risoe.dtu.dk and jrsun@g203.iphy.ac.cn

Abstract

We investigated the structure and magnetotransport properties of $Sm_{0.5}Ca_{0.5}MnO_3$ (SCMO) films epitaxially grown on (011)-oriented $SrTiO_3$ substrates, which exhibited clear charge/orbital ordering transition. A significant anisotropy of ~1000 in the colossal magnetoresistance (CMR) effect was observed in the films with a thickness between 50 and 80 nm, which was distinctly different from the basically isotropic CMR effect in bulk SCMO. The large anisotropy in the CMR can be ascribed to the intrinsic asymmetric strain in the film, which plays an important role in tuning the spin–orbit coupling in manganite films. The origin of the peculiar CMR effect is discussed.

(Some figures in this article are in colour only in the electronic version)

The intricate interlay of spin, charge, orbital and lattice degrees of freedom gives rise to versatile electronic phases and bicritical or multicritical behaviors in manganites [1], which also leads to the intrinsic strain resulting from lattice mismatch between the film and substrates, an effective factor for tuning the physical properties of manganite films [2–4]. In charge/orbital ordered (COO) manganites, in which the melting of COO insulating state generally results in a much larger colossal magnetoresistance (CMR) effect than that resulting from suppression of spin fluctuation near the Curie temperature in ferromagnetic manganites [5], the strain in (001)-oriented films always results in either a rather stable COO state or wiping out of the clear charge/orbital ordering transition of their bulk counterparts, and thus a much reduced CMR effect. The suppression of the charge/orbital ordering transition is ascribed to a biaxial-strain-induced tetragonal lattice distortion, whose stability restrains the original Jahn–Teller distortion upon cooling that is indispensable for formation of robust COO states. In contrast, the anisotropic strain relaxation process in the asymmetrically strained (011) films, which is much faster along the [0$\bar{1}$1] direction than that along the [100] one [6], permits the required Jahn–Teller-type lattice distortion in the bc plane [7]. As a result, clear charge/orbital ordering transitions have recently been realized in $Nd_{0.5}Sr_{0.5}MnO_3$ [7], $Pr_{0.5}Sr_{0.5}MnO_3$ [8, 9], $Bi_{0.4}Ca_{0.6}MnO_3$ [10, 11] and $La_{7/8}Sr_{1/8}MnO_3$ [12] films. On the other hand, the anisotropic strain results in versatile anisotropic physical properties due to strong coupling between the various degrees of freedom, such as the strain-correlated magnetic anisotropy in $La_{2/3}Ca_{1/3}MnO_3$ [6] and large anisotropy in electronic transport of $Bi_{0.4}Ca_{0.6}MnO_3$ films [13]. Since CMR is a magnetostriction-coupled phenomenon [14], the CMR effect may also be significantly affected by the strain in (011)-oriented films, especially when
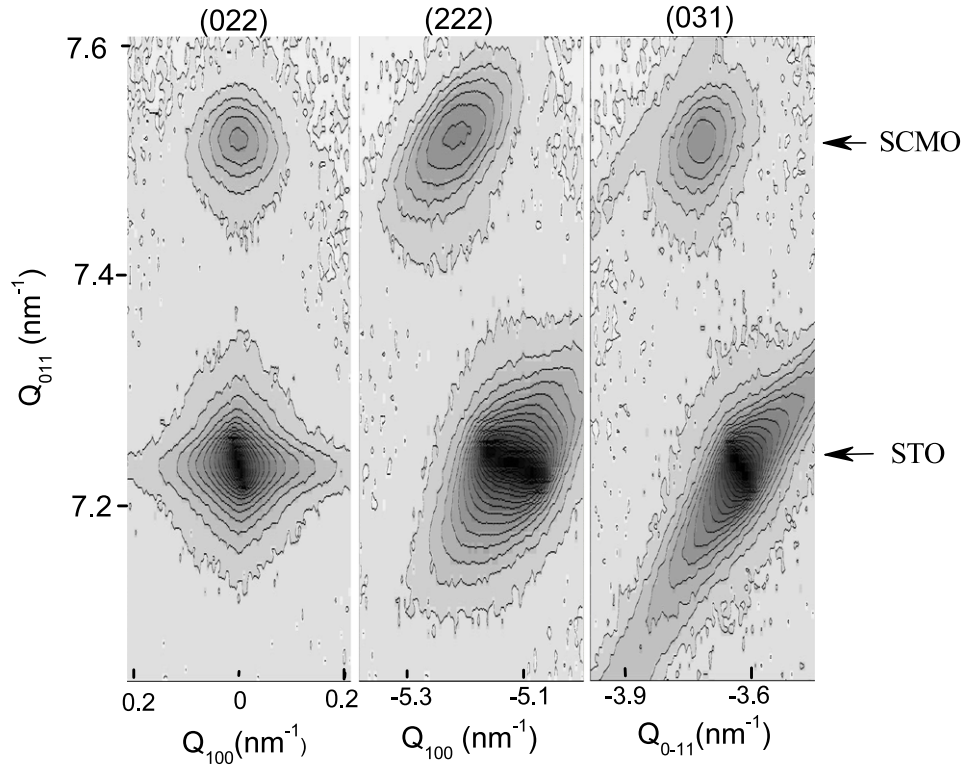
**Figure 1.** The reciprocal space maps around (022), (222) and (031) reflections for a 60 nm SCMO film.

it is partially or fully relaxed along one direction while strongly clamped, thus spatially confined and with no available magnetostriction, along the other direction. In this paper, besides the obvious charge ordering transition, a significant anisotropy in the CMR effect is observed in a (011)-oriented $Sm_{0.5}Ca_{0.5}MnO_3$ (SCMO) film.

SCMO films with a thickness t of 10–150 nm were grown on (011)-oriented $SrTiO_3$ (STO) substrates by pulsed laser deposition. During the deposition, the substrate temperature was kept at ~700 °C and the O_2 pressure at ~60 Pa. The structural properties of the films were analyzed by x-ray diffraction (XRD) and reciprocal space maps (RSMs) performed on a Bruker D80 Discover system. The films' surface morphology was analyzed by atomic force microscopy (AFM). Magnetic and transport measurements were performed with a Quantum Design superconducting quantum interference device (SQUID) magnetometer and a physical property measurement system (PPMS-14h), respectively. Resistivities along the in-plane [100] and [0$\bar{1}$1] directions, ρ_{100} and $\rho_{0\bar{1}1}$, respectively, were measured using the four-terminal method in a bridge-shaped sample (see the inset of figure 3(b)) patterned by a conventional photolithography and chemical etching technique, with dimensions of 0.1 mm in width and 0.4 mm in length which are sufficient to avoid phase separation effects.

Typical θ–2θ XRD scans of the films show that all the films are high textured with an out-of-plane direction of [011]. No other phases and textures were found. Figure 1 shows the RSMs around (022), (222) and (013) reflections for a 60 nm SCMO film. It is clearly shown that the film has good epitaxial growth on (011) STO substrates though the large lattice

mismatch between SCMO and STO (~3.3%). From the maps, $d_{011} \approx 0.2660$ nm, $d_{100} \approx 0.3839$ nm and $d_{0\bar{1}1} \approx 0.2691$ nm are obtained. Assuming that $b \approx c$, the lattice constants are determined to be $a \approx 0.3839$ nm, $b \approx c \approx 0.3784$ nm and $\gamma \approx 90.7°$ for the film. Thus, the in-plane asymmetry of the (011) substrate leads to a faster strain relaxation along the [0$\bar{1}$1] direction than that along the [100] direction compared with the situation in fully strained films, as discussed previously [6, 15]. In addition, $\gamma \neq 90°$ indicates a deviation of the SCMO unit cell from orthorhombicity, another peculiar strain-related effect in (011) manganite films [9, 10, 15].

For SCMO films grown on (001)-oriented substrates, it has been demonstrated experimentally that the biaxial strain wipes out the charge/orbital ordering transition [16]. In contrast, (011) films with $t \geqslant 80$ nm are found to exhibit a definite charge/orbital ordering transition at $T_{CO} \approx 235$ K as demonstrated in the clear increase in resistivity and the pronounced inflection in magnetization shown in the inset of figure 2(b). The clear phase transition becomes relatively broad with decreasing film thickness to 50 nm $< t <$ 80 nm due to the partially formed COO states, which is analogous to the case in $Bi_{0.4}Ca_{0.6}MnO_3$ films [15]. Similar to (001) SCMO films [16], the resistivity of the (011) films (50 nm $< t <$ 150 nm) decreases more than six orders under a high magnetic field ($\mu_0 H > 10$ T) and low temperature ($T < 100$ K) in addition to a six-times reduced critical magnetic field for melting the COO when compared to that of the bulk (60 T at 10 K) (figures 2(a) and (b)), which indicates a greatly depressed COO state and is consistent with the decreased T_{CO} (280 K for bulk). Surprisingly, further research reveals that
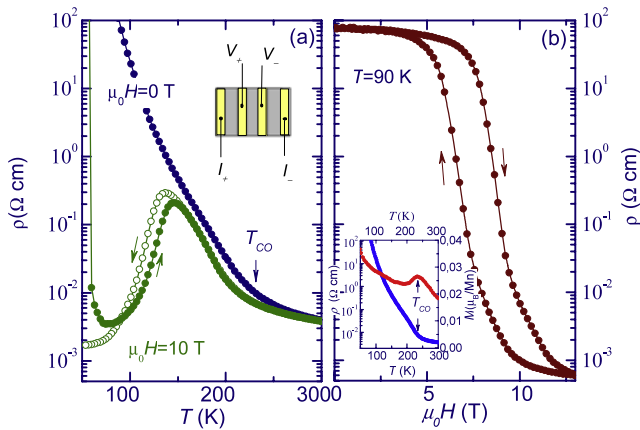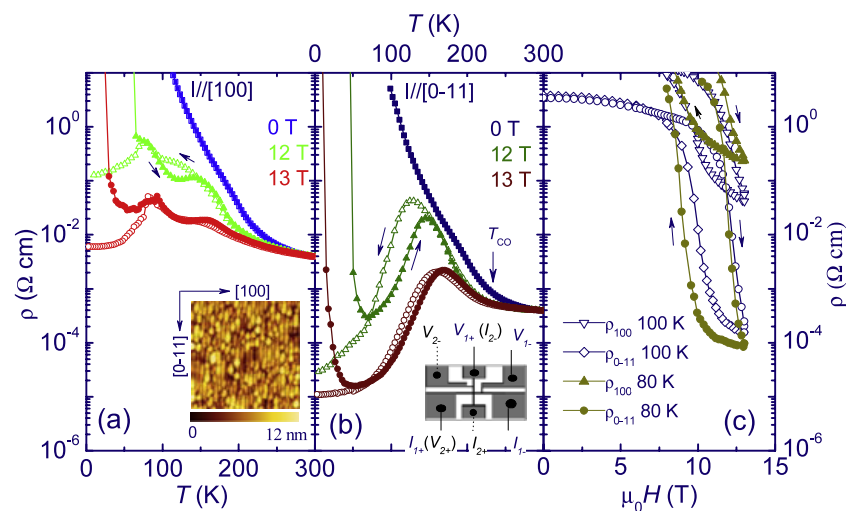
Figure 2. (a), (b) The temperature and magnetic field dependent resistivities of an 80 nm (011)-oriented SCMO film, respectively. Inset of (a): a schematic diagram of electrode contact geometry. Inset of (b): the temperature dependent resistivity and magnetization (measured at 2 T) for a 100 nm (011) film exhibiting robust charge/orbital ordering transition at T_{CO}.

the resistivities along the [100] and [0$\bar{1}$1] directions exhibit a dramatically different response to magnetic fields in the (011) SCMO films for 50 nm $< t <$ 80 nm.

Figures 3(a) and (b) show the temperature dependence of the resistivities ρ_{100} and $\rho_{0\bar{1}1}$, respectively, under a magnetic field of 0–13 T for a 60 nm SCMO film. Under 0 T, the film exhibits a large anisotropy of $\rho_{100}/\rho_{0\bar{1}1} \sim 10$ at 300 K, which also resembles the situation in Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ films [13]. Upon cooling, $\rho_{100}/\rho_{0\bar{1}1}$ decreases at $T < T_{CO}$ due to the faster increase in $\rho_{0\bar{1}1}$ resulting from its clearer charge/orbital ordering. As a result, ρ_{100}/ρ_{011} decreases to ∼5 at 100 K, below which the resistivity becomes too large to be measured. Under a magnetic field, the COO state is so robust that our maximal magnetic field of 13 T could hardly melt it at 5 K. Upon warming under 13 T, the collapse of the COO state

begins first at 15 K with resistivity reduced by a factor of more than 10^6 along the [0$\bar{1}$1] direction, while at 30 K the resistivity is decreased only by a factor of 10^3 along the [100] direction. Furthermore, little metallic behavior appears in ρ_{100}, though it exhibits a small decrease at $T < 80$ K during field cooling. An active metallic conducting behavior is seen at $T < 160$ K along the [0$\bar{1}$1] direction under 13 T. Obviously, the CMR effect of the SCMO film exhibits significant anisotropy, which is further confirmed in the magnetic field dependent resistivity results shown in figure 3(c).

The bulk SCMO exhibits a CE-type COO state, which generally melts to a ferromagnetic metal during the CMR effect. Such a CMR effect is basically isotropic with a little anisotropy due to the preferential occupation of e$_g$ orbits and their intrinsic anisotropy. The observed CMR effect in the SCMO films (50 nm $< t <$ 80 nm) is obviously different from the former conventional one. In addition, it should be noted that the large anisotropy in the CMR effect disappears in SCMO films with $t >$ 80 nm, whose behavior is like the bulk materials and exhibits no strain-induced transport anisotropy at $T > T_{CO}$ [13]. Thus, it turns out that the abnormal CMR effect exists only in the strongly strained SCMO films, which indicates that the abnormal CMR effect should also be a consequence of the strain effect. It is interesting to note that the large room temperature transport anisotropy and the significant anisotropic CMR in SCMO films is reminiscent of the bilayered manganites, such as (La$_{0.4}$Pr$_{0.6}$)$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$ [17], in which it was found recently that the Pr substitution-induced large decrease in the interlayer exchange coupling, with little change to the in-plane exchange coupling, plays an important role in the anisotropy of the CMR effect [18]. The spin–orbit coupling is the key issue in the CMR effect. The observed CMR anisotropy may also result from the anisotropy of the spin–orbit coupling effect. Moreover, a larger spin–orbital interaction along the [0$\bar{1}$1] direction compared with the [100] direction has been observed in (011)-oriented La$_{2/3}$Ca$_{1/3}$MnO$_3$ films through

Figure 3. (a), (b) The temperature dependence of ρ_{100} and $\rho_{0\bar{1}1}$, respectively, under magnetic fields of 0, 12 and 13 T for a 60 nm SCMO film. The arrows indicate charge ordering transitions. (c) The magnetic field dependent resistivities ρ_{100} and ρ_{0-11} at 80 and 100 K. Inset of (a): a 1 μm × 1 μm AFM image of the SCMO film with a mean-square-root-roughness of ∼2.1 nm. Inset of (b): a schematic diagram of the patterned sample and electrode contact geometries.

anisotropic magnetoresistance (AMR) and anomalous Hall effect measurements [19]. The anisotropy in the CMR effect here is obviously much larger than the AMR effect in ferromagnetic manganites [19, 20]; a significantly stronger spin–orbital coupling along the [0$\bar{1}$1] direction than that along the [100] direction is expected in SCMO films. Considering that the higher resistivity along [100] may mainly result from the reduced orbital overlap of the 3d and 2p electrons due to the strain imposed lattice expansion along a [13], the large anisotropic CMR effect may indicate that the stronger strained a also leads to a much decreased spin–orbit coupling along the [100] direction in (011) SCMO films.

As for the origin of the CMR effect in perovskite manganites, besides the conventional magnetic field-induced transition of the CE-type COO insulating state to a ferromagnetic metal phase, the magnetic-melting of the three-dimensional CE-type antiferromagnetic COO insulating state to a two-dimensional orbital ordered (OO) pseudometallic one (mainly an A-type layered antiferromagnetic structure or a C-type chainlike antiferromagnetic structure) could also result in a huge decrease in resistivity, which would further result in a large anisotropy in the CMR effect due to crossover in the transport dimension. Though such a crossover has been intensively predicted theoretically [21] and realized in bulk materials by tuning the one-electron bandwidth W or through band filling, such as that in $Pr_{0.5}(Sr_{1-y}Ca_y)_{0.5}MnO_3$ [22], no relevant phase transition induced by a magnetic field in CMR effect has been observed. The large anisotropy and 2D-like conductive behavior during the evolution of the CMR effect in SCMO films indicate the possible phase transition of the field-induced 3D COO state to a 2D conducting one. However, further evidence is needed to make the final determination.

In summary, a clear charge/orbital ordering transition was realized in $Sm_{0.5}Ca_{0.5}MnO_3$ films grown on (011)-oriented $SrTiO_3$ substrates. Furthermore, a peculiar CMR effect showing huge anisotropy was observed in SCMO films with a thickness between 50 and 80 nm, which can be ascribed to the intrinsic strain in the films. The results indicate that the anisotropic strain in manganite films makes it rather interesting to research the direction dependent responses of their physical properties to external stimuli, such as magnetic field, photo irradiation and pressure.

References

[1] Tokura Y 2006 *Rep. Prog. Phys.* **69** 797
[2] Barber Z H 2007 *J. Phys.: Condens. Matter* **19** 221001
[3] Abad L, Laukhin V, Valencia S, Gaup A, Gudat W, Balcells L and Martinez B 2007 *Adv. Funct. Mater.* **17** 3918
[4] Huijben M, Martin L W, Chu Y H, Holcomb M B, Yu P, Rijnders G, Blank D H A and Ramesh R 2008 *Phys. Rev. B* **78** 094413
[5] Sen C, Alvarez G and Dagotto E 2007 *Phys. Rev. Lett.* **98** 127202
[6] Infante I C, Sanchez F, Fontcuberta J, Wojcik M, Jedryka E, Estrade S, Peiro F, Arbiol J, Laukhin V and Espinos J P 2007 *Phys. Rev. B* **76** 224415
[7] Wakabayashi Y, Bizen D, Nakao H, Murakami Y, Nakamura M, Ogimoto Y, Miyano K and Sawa H 2006 *Phys. Rev. Lett.* **96** 017202
[8] Ogimoto Y, Takabo N, Nakamura M, Tamaru H, Izumi M and Miyano K 2005 *Appl. Phys. Lett.* **86** 112513
[9] Yin Z Z, Huang Z, Gao G Y, Wu W B, Wang G Y and Wang Y 2009 *J. Phys. D: Appl. Phys.* **42** 062004
[10] Kim D H, Christen H M, Varela M, Lee H N and Lowndes D H 2006 *Appl. Phys. Lett.* **88** 202503
[11] Chen Y Z, Sun J R, Wang D J, Liang S, Wang J Z, Han Y N, Han B S and Shen B G 2007 *J. Phys.: Condens. Matter* **19** 442001
[12] Chen Y Z, Sun J R, Wei A D, Lu W M, Liang S and Shen B G 2008 *Appl. Phys. Lett.* **93** 152515
[13] Chen Y Z, Sun J R, Liang S, Lu W M and Shen B G 2008 *J. Appl. Phys.* **104** 113913
[14] Mahendiran R, Ibarra M R, Maignan A, Millange F, Arulraj A, Mahesh R, Raveau B and Rao C N R 1999 *Phys. Rev. Lett.* **82** 2191
[15] Chen Y Z, Sun J R, Liang S, Lu W M, Shen B G and Wu W B 2008 *J. Appl. Phys.* **103** 096105
[16] Rauwei E, Prellier W, Mercey B, De Brion S and Chouteau G 2005 *J. Appl. Phys.* **98** 093903
[17] Apostu M, Suryanarayanan R, Revcolevschi A, Ogasawara H, Matsukawa M, Yoshizawa M and Kobayashi N 2001 *Phys. Rev. B* **64** 012407
[18] Moussa F, Hennion M, Gukasov A, Petit S, Regnault L P, Ivanov A, Suryanarayanan R, Apostu M and Revcolevschi A 2008 *Phys. Rev. B* **78** 060406(R)
[19] Bibes M, Laukhin V, Valencia S, Martínez B, Fontcuberta J, Yu Gorbenko O, Kaul A R and Martínez J L 2005 *J. Phys.: Condens. Matter* **17** 2733
[20] Donnell J O, Eckstein J N and Rzchowski M S 2000 *Appl. Phys. Lett.* **76** 218
[21] Pradhan K, Mukherjee A and Majumdar P 2007 *Phys. Rev. Lett.* **99** 147206
[22] Smolyaninova V N, Biswas A, Hill C, Kim B G, Cheong S W and Greene R L 2003 *J. Magn. Magn. Mater.* **267** 300