Anisotropic strains and magnetoresistance of La$_{0.7}$Ca$_{0.3}$MnO$_3$

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Abstract

Thin films of perovskite manganite La$_{0.7}$Ca$_{0.3}$MnO$_3$ were grown epitaxially on SrTiO$_3$(100), MgO(100) and LaAlO$_3$(100) substrates by the pulsed laser deposition method. Microscopic structures of these thin film samples as well as a bulk sample were fully determined by x-ray diffraction measurements. The unit cells of the three films have different shapes, i.e., contracted tetragonal, cubic, and elongated tetragonal for SrTiO$_3$, MgO, and LaAlO$_3$ cases, respectively, while the unit cell of the bulk is cubic. It is found that the samples with cubic unit cell show smaller peak magnetoresistance than the noncubic ones do. The present result demonstrates that the magnetoresistance of La$_{0.7}$Ca$_{0.3}$MnO$_3$ can be controlled by lattice distortion via externally imposed strains.
The compounds of mixed valence manganite with the perovskite structure, La$_{1-x}$D$_x$MnO$_3$ with D for a divalent metal ion, have attracted renewed attention due to their anomalously large negative magnetoresistance (MR) effects [1–4]. While these manganites are paramagnetic insulators at high temperatures, a compound with $0.2 < x < 0.4$ shows a simultaneous appearance of metallic conduction and ferromagnetism below a certain ordering temperature $T_c$, around which the large MR effect is found [5,6]. (Resistance at zero field reaches a maximum at $T_p \approx T_c$.) As a function of composition high $T_c$ and large values of MR are usually achieved in a sample with $x \approx 0.3$, which is thus of particular interest.

Zener’s double exchange model (DEM) accounts for ferromagnetic ordering in this system in terms of the itinerancy of charge carriers, which is characterized by the Mn to Mn hopping matrix element, $t = t_0 \cos \theta/2$ where $\theta$ is the angle between the core spins at nearest Mn sites and $t_0$ is the bare matrix element [7]. The $\theta$ dependence of $t$ gives rise to negative magnetoresistance. However, recent theories have emphasized the importance of the polaron effect associated with dynamic Jahn-Teller distortion of Mn$^{3+}$ [8]. Band structure calculations for the D=Ca system indicate the half-metallic nature and strong Mn-O hybridization for the majority band; this unusual band structure was suggested as the reason for magnetoresistive behaviors [9].

Due to numerous potential applications of large MR materials, such as magnetic recording, sensors, and switching devices, the major research focus of mixed valence manganites has been on increasing the value of MR and shifting the MR peak above room temperature. However, tailoring the materials for optimum conditions in the sensitivity and temperature variation of the magnetoresistive response would require the basic understanding of transport phenomena in the system. In this regard, it would be of value to carefully examine their properties as a function of lattice strain. The DEM, for example, naturally predicts a dependence of magnetic and transport properties on $t$, which in turn would depend on lattice constant. Furthermore, Pickett and Singh’s calculation [9] identified lattice distortion as an important factor in determining the band structures of the system.

Previous studies of the lattice effects on magnetotransport properties of perovskite man-
ganites include two cases: first, the average radius of trivalent A-site ions was changed by mixing two kinds of ions of different radius, for example, La and Pr, while keeping the divalent ion concentration $x$, which determines the carrier density, fixed. Then the variation of the trivalent A-site radius would cause internal stresses (chemical pressure) in the system [10,11]. When this average radius is reduced, it turned out that $T_p$ is decreased and the magnitude of MR is enhanced. While Hwang et al. interpreted these results in terms of Mn-O-Mn bond angle variation, it is quite obvious that the whole effect cannot be attributed solely to the geometrical lattice effects and the chemical origin must be taken into account [12]. The second kind of experiments were conducted by applying an external hydrostatic pressure [13–15]. The application of hydrostatic pressure increases $T_p$ monotonically and strongly suppresses the magnitude of MR. In these cases, the pressure range was limited and no strain data were reported.

Thus, the current situation calls for systematic investigations on the pure lattice effects on the magnetotransport properties of perovskite manganites in the absence of chemical interference; in particular, the effects of anisotropic strains would be of great interest. For this purpose, we utilized the fact that the lattice parameters of films are different from that of a bulk and can be varied by depositing films on various substrates. We were able to vary the lattice symmetry as well as the lattice constants of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ (LCMO) thin films. For the first time to our knowledge it is revealed that crystal symmetry is an important factor in controlling magnetotransport properties of LCMO.

LCMO bulk samples were prepared by the standard solid state reaction technique from 99.9% purity oxide and carbonate powders. After repeated grinding and calcining at 1000°C for 24 h, cold isostatic pressed pellets were sintered at 1350°C for 5 h in air. The X-ray diffraction analysis of the pellets showed the single phase perovskite structure of cubic symmetry with lattice constant $a = 3.867$ Å. Using these pellets as a target, thin films of LCMO were grown on $\text{SrTiO}_3(100)$, $\text{MgO}(100)$, and $\text{LaAlO}_3(100)$ substrates by the pulsed laser deposition method under the same growth conditions. Substrate temperature was controlled at 650 °C, and oxygen partial pressure was maintained at 150 mtorr during the deposition.
period. After deposition, the films were left at 650 °C for 10 min under an oxygen pressure of 1 torr, and then freely cooled to room temperature. The typical thickness of the films was approximately 1000 Å. Resistance and magnetoresistance of the LCMO samples, in the film and bulk form, were measured by the four-probe method as a function of temperature (T) and magnetic field (B). T was varied from 50 K to 320 K, and B was changed up to 1 T. The direction of the applied field was parallel to that of the probing current. Measurements of magnetic susceptibility and magnetization were also performed using an ac susceptometer and a vibrating sample magnetometer, respectively. These measurements verified the ferromagnetic phase transition in the samples which accompanies the resistance maximum [16].

4-circle x-ray diffractometry (CuKα source) was used to characterize the microscopic structure of the films at room temperature, and confirmed their epitaxial nature. The diffraction peaks were precisely determined by fitting the split Kα1 and Kα2 lines with the two-Gaussian functional form. The lattice constant of elementary perovskite cell along the film/substrate normal direction, c_p, was obtained from the position of (001) peaks of θ-2θ scans, while the in-plane lattice constants, a_p≈b_p, were determined by analyzing the (203) and (104) off-normal peaks. Table I summarizes x-ray diffraction results for the films. The result for the bulk target, which is cubic, is also included. It should be noticed from the table that the lattice symmetry of the films changes from contracted tetragonal (the SrTiO₃ case) to nearly cubic (the MgO case) and to elongated tetragonal one (the LaAlO₃ case) as unit cell volume V_p decreases; this behavior is due to the biaxial nature of strains inherent in films [17,18].

With these structural information in hand, we present the results of transport measurements. In Fig. 1 plotted is the resistance at B= 0 and 1 T of the three LCMO films, normalized to their respective room temperature values, versus T. As is easily seen from the figure, T_p, the maximum resistance temperature at zero field, shifts to a higher temperature and the peak value of resistance decreases with reduction in unit cell volume. Apparently this behavior resembles that of a bulk under a hydrostatic pressure mentioned above [13, 13].
However, there exists a clear distinction in the MR behaviors; in the inset of Fig. 1 shown is the MR, defined as 
\[
\frac{R(0) - R(B = 1T)}{R(0)}
\]
of the films. The striking feature in the figure is that the maximum MR, which occurs at approximately 15 K below \( T_p \), is not monotonic as a function of unit cell volume. In fact, the film with nearly cubic unit cell (one deposited on MgO) displays a smaller value in the maximum MR than the other two films. This is in sharp contrast to the bulk behavior where the reduction in unit cell volume (or increasing hydrostatic pressure) gives rise to a monotonic decrease of the maximum MR, in conjunction with the monotonic \( T_p \) rise \([13,14]\).

To directly expose the correlation between the lattice structure and the magnetotransport properties of LCMO, \( T_p \) and the maximum MR values of both the films and the bulk are plotted against unit cell volume in Fig. 2. The nonmonotonic dependence of these properties on unit cell volume is indeed evident. It is particularly clearly manifested in the MR behavior, where the samples with cubic symmetry (middle two points in the figure) show lower values than the noncubic ones (outer two points) do. \( T_p \) also varies nonmonotonically, but in somewhat different fashion. \( T_p \) increases from the lowest value for the sample with the largest cell volume (the one on SrTiO\(_3\) with tetragonal symmetry), as the volume decreases; after reaching a maximum at the bulk sample (with the cubic cell), \( T_p \) starts to decrease. This \( T_p \) behavior may be interpreted as a superposition of two differing tendencies: one tendency is related to the volume effect favoring the monotonic increase of \( T_p \) as the volume of unit cell is reduced. Notably this volume effect seems to be lacking in MR. The other tendency is due to the symmetry effect, in accord with the MR behavior, favoring the maximum \( T_p \) for cubic samples. From these observations one can conclude that the lattice symmetry, in addition to the unit cell volume, plays a crucial role in determining magnetotransport properties of LCMO. The symmetry change seen in the film samples would not arise in the case of a cubic bulk under hydrostatic pressure where isotropic strains prevail.

The DEM may offer some qualitative explanation of the present results, that is, the bare matrix element \( t_0 \) in \( t(t_0 \cos \frac{\theta}{2}) \) is made to include a structural dependence. Since it is known that the band width of a perovskite material depends on the bond length \([13]\) as well
as the bond angle, \( t_0 \) may be expressed as \( t_0 \sim \frac{\cos \phi}{d} \), where \( d \) is the Mn-O bond length and \( \phi \) is the deviation of the Mn-O-Mn bond angle from 180°. While the volume of unit cell is expected to depend more directly on \( d \), the noncubic nature of symmetry would be closely related to the bond angle parameter \( \phi \). However, the symmetry effect in MR may not be accounted for solely in this model. It is worthwhile, in this regard, to recall that the band structure of the LCMO system and its half metallic nature depend sensitively on lattice distortion, while the volume variation is of less importance. It is also noteworthy that the externally imposed tetragonal distortions lift the orbital degeneracy which is essential for the dynamic Jahn-Teller effect. In summary, our results thus have important implications on the current understanding of ferromagnetic manganites, besides demonstrating that the MR of LCMO may be controlled by external anisotropic strains.

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FIGURES

FIG. 1. Resistivity of La$_{0.7}$Ca$_{0.3}$MnO$_3$ thin films on SrTiO$_3$(100), MgO(100), and LaAlO$_3$(100) is plotted as a function of temperature ($T$) and field ($B$). Resistivity of each sample is normalized to the value at $T = 317$ K and zero field. No appreciable thermal hysteresis was found in the measurements and the data obtained in cooling are displayed. In the inset shown is magnetoresistance, defined as $[R(0) - R(B = 1T)]/R(0)$, of the films.

FIG. 2. Peak resistance temperature $T_p$ at zero field (circles) and maximum MR (squares) are plotted against the unit cell volume $V_p$. The solid symbols denote the data for the films, and the empty ones do those for the bulk. Note the symmetry change as the volume varies. The unit cells of the samples depicted by the middle two points are cubic, while the outer two points represent the samples with tetragonal symmetry. The lines are guides for the eye.
TABLES

TABLE I. Lattice parameters ($a_p$, $b_p$, $c_p$) and unit cell volume ($V_p$) of LCMO samples obtained from x-ray diffraction measurements at room temperature. The lattice parameters represent the elementary perovskite unit cell. Thin films are designated by substrates.

| Substrate       | Cubic a (substrate, Å) | $a_p \approx b_p$ (LCMO in-plane, Å) | $c_p$ (LCMO normal, Å) | $V_p$ (Å$^3$) |
|-----------------|-------------------------|--------------------------------------|------------------------|--------------|
| LaAlO$_3$(100)  | 3.794                   | 3.842                                | 3.878                  | 57.24        |
| LCMO Target     |                         | 3.867                                | 3.867                  | 57.83        |
| MgO(100)        | 4.216                   | 3.885                                | 3.891                  | 58.73        |
| SrTiO$_3$(100)  | 3.895                   | 3.921                                | 3.845                  | 59.11        |
