Strain effect on electronic transport and ferromagnetic transition temperature in La$_{0.9}$Sr$_{0.1}$MnO$_3$ thin films

X. J. Chen
Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany
and Department of Physics, Kent State University, Kent, OH 44242, USA

S. Soltan, H. Zhang, and H.-U. Habermeier
Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany
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We report on a systematic study of strain effects on the transport properties and the ferromagnetic transition temperature $T_c$ of high-quality La$_{0.9}$Sr$_{0.1}$MnO$_3$ thin films epitaxially grown on (100) SrTiO$_3$ substrates. Both the magnetization and the resistivity are critically dependent on the film thickness. $T_c$ is enhanced with decreasing the film thickness due to the compressive strain produced by lattice mismatch. The resistivity above 165 K of the films with various thicknesses is consistent with small polaronic hopping conductivity. The polaronic formation energy $E_P$ is reduced with the decrease of film thickness. We found that the strain dependence of $T_c$ mainly results from the strain-induced electron-phonon coupling. The strain effect on $E_P$ is in good agreement with the theoretical predictions.

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I. INTRODUCTION

The discovery of colossal magnetoresistance effect in epitaxial manganite thin films has renewed interest in the doped manganite perovskite materials Ln$_{1-x}$B$_x$MnO$_3$ (Ln=trivalent rare-earth ions; B=divalent alkaline-earth ions) for potential sensor and magnetic recording applications as well as the need to understand the mechanisms underlying their behavior. It has been found that properties such as ferromagnetic transition temperature $T_c$, resistivity $\rho$, and magnetoresistance are sensitive to the epitaxial strain due to lattice mismatch of the film with substrate. When the film is grown on the substrate whose lattice parameter is smaller or larger than that of the bulk material, the epitaxial strain is expected to be compressive or tensile, respectively. Compressive strain usually reduces the resistivity and shifts $T_c$ towards the higher temperature. These effects have been confirmed in La$_{0.7}$Ca$_{0.3}$MnO$_3$ films and La$_{0.7}$Sr$_{0.3}$MnO$_3$ films grown on various substrates.

The observed strain effect is usually interpreted qualitatively within double exchange model since the hopping matrix element $t$ could be altered by epitaxial strain through changing the Mn-O bond length $d$ and the Mn-O-Mn bond angle $\theta$. It has also been proposed that the Jahn-Teller electron-phonon coupling plays an important role in strain effect on $T_c$. However, recent detailed studies show that compressive strain does not always lead to enhancement of $T_c$ while the cationic vacancies due to the oxygen annealing significantly enhance the $T_c$ values much higher than any bulk values in the series compounds. In most cases, tensile strain suppresses ferromagnetism and reduces $T_c$ in manganite films. But some anomalous results have also been reported, showing $T_c$ enhanced by tensile strain. Most interestingly, there are reports of multiple phase segregation in fully strained epitaxial films. The ferromagnetic coupling within the metallic regions accounts for the changes of $T_c$ and conductivity. Thus, the strain effect in manganite films is far from being fully understood and challenging.

Lightly doped La$_{1-x}$Sr$_x$MnO$_3$ shows a great variety of intriguing phenomena originating from a pronounced interplay between spin, lattice, charge, and orbital degrees of freedom. As a result, many phenomena like charge order, orbital order, and phase separation have been recently observed in this regime of the phase diagram. La$_{0.9}$Sr$_{0.1}$MnO$_3$ is in the phase boundary of a spin-canted antiferromagnetic insulator and a ferromagnetic insulator. This material has the lowest $T_c$ among the series compounds which makes it possible to perform systematic investigations of the resistivity in the paramagnetic regime over a broad temperature range without using specialized equipment to extend the temperature range. Meanwhile, the pressure derivative of $T_c$, $dT_c/dP$, in this material is highest among the manganite perovskites.

It has been generally believed that pressure changes $T_c$ and $\rho$ in a similar manner as epitaxial strain. Thus, transport properties, transition temperatures, and phase transitions are expected to be significantly affected by epitaxial strain in the La$_{0.9}$Sr$_{0.1}$MnO$_3$ films. Moreover, these investigations are most important for the understanding of the fruitful phenomena and the use of these films as magnetic devices as well as electrodes in high-temperature solid oxide fuel cells.

In this work we investigate the transport properties by measuring resistivity and magnetization of the epitaxial La$_{0.9}$Sr$_{0.1}$MnO$_3$ films on SrTiO$_3$. The data clearly show that the high-temperature resistivity of the films can be well ascribed by a model for small-polaron hopping in the adiabatic limit. We experimentally find that the small polaronic formation energy $E_P$ decreases with
the reduction of the film thickness, which can account for the strain effect on $T_c$. We suggest that the electron-phonon coupling is responsible for the strain effect on the high-temperature electronic transport and the ferromagnetic transition temperature.

II. EXPERIMENTAL DETAILS

Thin films of La$_{0.9}$Sr$_{0.1}$MnO$_3$ were grown using the pulsed laser deposition technique. The target used had a nominal composition of La$_{0.9}$Sr$_{0.1}$MnO$_3$. The substrates were (100) single crystal of SrTiO$_3$. The laser energy density on the target was 2 mJ/cm$^2$ and the ablation rate was 5 Hz. The substrates were kept at a constant temperature of 850$^\circ$C during the deposition which was carried out at a pressure of 0.40 mbar of oxygen. The films were in situ annealed at 940$^\circ$C in oxygen at 1.0 bar for 30 minutes. This procedure always results in films of high crystalline quality and in very sharp film-substrate interfaces. The thickness of the films was varied from 200 to 2000 Å as measured by Dektak. The chemical composition of the films was determined by microprobe analysis, which showed a (La,Sr)/Mn ratio of 1:1 and a Sr content of $x = 0.10 \pm 0.01$.

The structural study was carried out by x-ray diffraction (XRD) at room temperature by a Rigaku x-ray diffractometer with a rotating anode and Cu Kα radiation, $\lambda = 1.5406$ Å. The resistivity $\rho$ was measured from unpatterned samples with sputtered chromium gold contacts using a standard four-probe technique. Magnetization $M$ was recorded in a magnetic field parallel to the film plane using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer as a function of temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the evolution of the room temperature XRD data for La$_{0.9}$Sr$_{0.1}$MnO$_3$ thin films with thicknesses from 200 to 2000 Å. Each sample is single crystal and (100) oriented without other impurity phases. Above $T = 105 \text{ K}$, SrTiO$_3$ has a perfect cubic perovskite structure with a lattice parameter $a = 3.905$ Å. La$_{0.9}$Sr$_{0.1}$MnO$_3$ has a distorted perovskite structure due to the tilting of the MnO$_6$ octahedra and the Jahn-Teller distortion, which results in a slightly orthorhombic structure. The bulk lattice parameters for this compound at room temperature are $a = 5.5469$ Å, $b = 5.56033$ Å, and $c = 7.7362$ Å. The in-plane lattice mismatch between the film and the substrate is given by $\epsilon = |d_{\text{film}} - d_{\text{substrate}}|/d_{\text{bulk}}$ with $d$ a lattice parameter. Epitaxially grown La$_{0.9}$Sr$_{0.1}$MnO$_3$ film on (100) SrTiO$_3$ substrates are under compressive strain since $d_{\text{bulk}} > d_{\text{strained}}$ with the bulk value $d_{\text{bulk}} = 3.927$Å. With decreasing the film thickness, the in-plane lattice parameter of the film decreases and the compressive strain is then enhanced.

Figure 2 shows the temperature dependence of the magnetization measured in 0.5 T of the films with various thicknesses, after correction for the magnetization of the substrate. The curves have been measured by warming up in the magnetic field after zero field cooling. The features of the $M - T$ curves are ferromagnetic with $M \approx 230 - 360$ emu/cm$^3$ at 10 K. The magnetization was taken at 0.5 T to avoid the variation due to magnetic domain rotation at lower fields. Both $T_c$ and $M$ increase with decreasing the film thickness. The value of $T_c$ for 200 Å thin film is 50 K higher than the bulk value. We had not observed a magnetization jump occurring at a characteristic temperature $T_{MI}$ as appeared in the La$_{0.9}$Sr$_{0.1}$MnO$_3$ single crystals which indicates a canted antiferromagnetic state as confirmed by neutron scattering experiments. This is not surprising since the strained films usually show properties much different from the bulk compounds in manganites.

Although the reduction of film thickness should enhance $T_c$ under compressive strain as we observed in Fig. 2, there are few measurements in other manganites to support this phenomenon. The experiments on La$_{0.8}$Ca$_{0.2}$MnO$_3$ films grown on LaAlO$_3$ do not always show a correlation between the compressive strain and $T_c$. Interestingly, anomalously high $T_c$ and metal-insulator transition temperature $T_{MI}$ (100 K higher than bulk values) have been observed in this strained film with 1000 Å thickness after annealing under oxygen. For this La$_{0.8}$Ca$_{0.2}$MnO$_3$ film, $T_{MI}$ is 30 K higher than the highest $T_{MI} = 260$ K found for $x = 0.33$ bulk compound. Thus, the large enhancement of $T_c$ and $T_{MI}$ in this film should be dominated by compressive strain. The lack of this enhancement observed previously in La$_{0.8}$Ca$_{0.2}$MnO$_3$ thin film may be due to oxygen deficiency.

The results of the temperature dependence of the re-
The resistivity of our films displays semiconducting behavior at high temperatures, and metallic behavior for $T_{CA}$, $T_s$ ≤ $T ≤ T_{MI}$. It has an up-turn at $T_{CA}$, and then becomes of semiconducting character. The neutron scattering study demonstrates that the point of resistivity up-turn is consistent with the onset temperature of the polaron order. The magnitude of resistivity of our films is smaller than those of the single crystals. For example, the resistivity of the 200 Å film at $T = 100$ K is 83.7 $\Omega$ cm. Note that the compressive strain decreases the resistivity in our thin films. This behavior is typical for manganites films under compressive strain. The observed $T_{MI}$ (defined as the temperature where $d\rho/dT$ changes sign) of $\sim$ 100 - 150 K in our films are comparable to those of La$_{0.9}$Sr$_{0.1}$MnO$_3$ single crystals. For films with thicknesses $d = 750$ and 2000 Å, $T_{MI}$ almost coincides with $T_s$. However, $T_{MI}$ is significant smaller than $T_s$ for the ultrathin films. The scenario to correlate with this observation could be the existence of microscopic phase segregation due to the formation of small ferromagnetic clusters, which are large enough to give a magnetic contribution in ultrathin films but not to allow metallic conductivity appearing in zones of ferromagnetic insulating behavior. The smaller $T_{MI}$ value compared to $T_s$ has reported previously in La$_{0.67}$Sr$_{0.33}$MnO$_3$ thin films. Recent nuclear magnetic resonance measurements in La$_{2/3}$Ca$_{1/3}$MnO$_3$ films on SrTiO$_3$ give strong evidence in favor of the existence of microscopic phase separation.

Additional increase of resistivity on cooling can be seen at low temperatures preceded by a minimum at $T_{CA}$. The structural data of single crystals show that a phase transformation from a pseudocubic $O''$ type to an orthorhombic $O'$ type structure occurs near $T_{CA}$. The low-temperature phase is known to be a spin-canted antiferromagnetic phase for $0 \leq x \leq 0.1$, which results from competing antiferromagnetic superexchange interaction between half-filled $t_{2g}$ orbitals along the c axis Mn-O-Mn bonds and ferromagnetic double-exchange interaction via $e_g$ conduction electrons. With the reduction of the film thickness, $T_{CA}$ shifts towards low temperatures and $\rho$ decreases in the insulating low-temperature phase. It has been reported that $T_{CA}$ increases and $\rho$ decreases under pressure in La$_{0.9}$Sr$_{0.1}$MnO$_3$ single crystals. Although $\rho$ behaves in a similar manner under compressive strain and external pressure, the observed variation of $T_{CA}$ is in sharp contrast with the pressure measurements. It has been established that pressure influences $T_{CA}$ in the same way as an increase in $x$ with a maximum within the range $0.12 < x < 0.15$ for the slightly doped La$_{1-x}$Sr$_{x}$MnO$_3$. At low-pressures, the thermoelectric power through $T_{CA}$ is sensitive to the charge carrier density. It is indicated that pressure induces the change of carrier concentration, which should account for the dependence of $T_{CA}$ on pressure. The growth conditions such as film deposition and oxygen annealing are same for all films studied here. The carrier concentration in these films should not be different. Therefore, the dependence of $T_{CA}$ on strain is possibly different from the pressure effect on $T_{CA}$.

An interesting feature is the absence of the jump in resistivity in films near $T \sim 330$ K. The structural analyses on La$_{0.9}$Sr$_{0.1}$MnO$_3$ crystals revealed that system undergoes another structural transition around characteristic temperature $T_s = 330$ K from an orthorhombic $O$ phase having a dynamic Jahn-Teller distortion to an orthorhombic $O'$ phase at lower temperatures where Jahn-Teller distortion becomes static and cooperative. The jump in resistivity at $T_s$ in single crystals has been reported by Urushihara et al. The absence of the jump indicates that the compressive strain in films either suppresses the structural phase transition or shifts $T_s$ towards higher temperatures above 350 K. There is competition between the charge mobility and the structural phase transition in the slightly doped La$_{1-x}$Sr$_x$MnO$_3$. 

![FIG. 3: Temperature dependence of resistivity of La$_{0.9}$Sr$_{0.1}$MnO$_3$ films with various thicknesses.](image-url)
The change tendency of $T_s$ and $T_{CA}$ is usually different under pressure or magnetic field. In our films, $T_{CA}$ decreases with decreasing film thickness due to the compressive strain. Thus, the increase of $T_s$ is possible under compressive strain.

The preconditions for polaron formation, namely, large electron-lattice coupling and low electronic hopping rates, appear to be satisfied for manganites. We have represented ln($\rho$/T) versus inverse temperature. A linear behavior is obtained between 165 and 350 K. This is strong support of the mechanism of adiabatic small polaron conduction. The resistivity as a result of hopping of adiabatic small polarons is, within the Emin and Holstein theory,[3] given by

$$\rho = AT \exp \left( \frac{E_A}{k_B T} \right).$$

Here the prefactor $A$ depends on the polaronic concentration, the hopping distance, and the frequency of the longitudinal optical phonon. The activation energy $E_A$ has the form $E_A = E_F/2 + \epsilon_0 - J$, where $\epsilon_0$ is the energy required to generate intrinsic carriers and $J$ is the transfer integral.

From the fit to Eq. [1], the values of $A$ and $E_A$ are obtained. These data are summarized in Table I. The fitting for $\rho$ is valid for temperatures larger than half the Debye temperature $\Theta_D$. This is fulfilled for the present films since specific heat measurements show $\Theta_D$ in the 255 – 360 K range. We noted that the fitting adiabatic prefactor $A$ is in the range from 1.19×10$^{-6}$ to 2.39×10$^{-6}$ Ω cm/K, which is typical for small polaronic conduction as observed in La$_{0.67}$Ca$_{0.33}$MnO$_3$ films[30] as well as (La$_{1-x}$Gd$_x$)$_{0.67}$Ca$_{0.33}$MnO$_3$ films.[31]

There have been studies of high-temperature resistive behavior in La$_{0.9}$Sr$_{0.1}$MnO$_3$ bulk materials.[33,34,44] The reported conduction mechanism are controversial. Early measurements on the ceramic La$_{0.9}$Sr$_{0.1}$MnO$_3$ show that the high-temperature resistivity obeys the small polaron transport behavior in the nonadiabatic limit with an activation energy $E_A = 0.2$ eV.[44] In single crystals, some groups found that their data can be well fitted by variable-range-hopping model $\rho = \rho_0(T/T_0)^{1/2}\exp[(T_0/T)^{1/4}]$ with $T_0 = 1.72 \times 10^8$ K in the paramagnetic regime[43] while others[44] reported the resistivity follows a small polaron model in the adiabatic limit above $T_{MI}$ with activation energy $E_P = 0.3$ eV. The high-temperature resistivity of our films with various thicknesses is consistent with adiabatic small polaron hopping conductivity. It has been generally accepted that the conductivity can be well ascribed by adiabatic small polaron model in La$_{1-x}$Ca$_x$MnO$_3$ films.[33,34,44] Our present data provide clear support for the existence of this conductivity mechanism in La$_{1-x}$Sr$_x$MnO$_3$ films.

At high temperatures and in the adiabatic limit the contribution from $\epsilon_0$ and $J$ may be neglected, the variation of $E_P$ is approximately affected by the change of $E_A$. Taking $E_P = 2E_A$, we have plotted the thickness dependence of $E_P$ in Fig. 4. The thickness dependence of $T_s$ is also plotted for comparison. It is interesting to notice that the variation of $T_s$ with thickness can be well reflected by the thickness dependence of $E_P$. For the thick films, the strain is relaxed. Both $T_s$ and $E_P$ scarcely change with the thickness. Below 750 Å, with the reduction of film thickness, $E_P$ decreases, whereas $T_s$ increases. It is therefore indicated that the electron-phonon coupling possibly dominates the strain effect on $T_s$.

The polaronic formation energy $E_P$ is usually related to the effective bandwidth $W_{eff}$ in polaronic models. Zhao et al.[45] proposed an effective bandwidth of the form $W_{eff} = W \exp(-\gamma E_P/\hbar \nu)$, where $W$ is the electronic “bare” bandwidth, $\nu$ is the characteristic vibration frequency of the optical phonon mode, and $\gamma$ depends on the ratio $E_P/W$. According to the model proposed by Varma,[46] $T_c$ can be written as

$$T_c = \frac{0.1}{2} \frac{W}{n \hbar \nu} \exp \left( \frac{\gamma E_P}{\hbar \nu} \right) n (1 - n),$$

where $n$ denotes the carrier concentration. Considering that $\nu$ is related to the isotope mass $M$ through $\nu \propto M^{-1/2}$, the oxygen isotope exponent $\alpha \equiv 4/

| Thickness (Å) | $E_A$ (meV) | $A$ (10$^{-6}$ Ω cm/K) | $T_c$ (K) |
|---------------|-------------|----------------|--------|
| 200           | 119.1       | 1.86           | 194.9  |
| 300           | 124.8       | 1.28           | 150.0  |
| 400           | 126.8       | 1.19           | 116.9  |
| 750           | 139.6       | 1.28           | 100.0  |
| 2000          | 141.3       | 2.39           | 105.6  |
FIG. 5: Thickness dependence of the ferromagnetic transition temperature $T_c$ (circles) and the polaronic formation energy $E_P$ (triangles) in La$_{0.9}$Sr$_{0.1}$MnO$_3$ films.

$-d \ln T_c/d \ln M$ is then given by $\alpha = 0.5 \gamma E_P/h \nu$. The strain coefficient of $T_c$, $d \ln T_c/d \epsilon$, is readily obtained from Eq. (2)

$$
\frac{d \ln T_c}{d \epsilon} = \frac{d \ln W}{d \epsilon} - 2 \frac{d \alpha}{d \epsilon} .
$$

(3)

For La$_{0.9}$Sr$_{0.1}$MnO$_3$, the pressure coefficient of $T_c$ has been found by Senis et al. to be $d \ln T_c/dP = 0.16$ GPa$^{-1}$. Using the lattice compressibility $K_a = 2.32 \times 10^{-3}$ GPa$^{-1}$ we obtain $d \ln T_c/dP = 69$. The electronic bandwidth $W$ of the manganites can be estimated by the average Mn–O bond distance $d$ and the Mn-O-Mn angle $\theta$ by using the relation $W \propto \cos \phi/d^{1.5}$, where $\phi = (\pi - \theta)/2$. The pressure dependence of $\cos \phi$ has been determined by neutron diffraction measurements to be $(\cos \phi)^{-1}d \cos \phi/dP = 2.1 \times 10^{-4}$ GPa$^{-1}$. Taking the value of $K_a$ as the bond compressibility $K_d$, the calculated $d \ln W/dP$ is 3.6. Thus, $d \alpha/d \epsilon = -32.7$ is obtained from Eq. (3). In La$_{0.9}$Sr$_{0.1}$MnO$_3$, the oxygen isotope exponent $\alpha = 0.2$ reported previously by Zhao et al. Based on the above determined parameters, one estimated the pressure derivate of $\alpha$, $d \alpha/d \epsilon = -0.076$ GPa$^{-1}$. This value is very close to the reported value of $-0.05$ GPa$^{-1}$ in La$_{0.65}$Ca$_{0.35}$MnO$_3$.

According to the expression for $\alpha$, $d \alpha/d \epsilon$ is then expressed as

$$
\frac{d \alpha}{d \epsilon} = \alpha \left( \frac{d \ln E_P}{d \epsilon} - \frac{d \ln \nu}{d \epsilon} \right) .
$$

(4)

The Raman spectra of La$_{0.9}$Sr$_{0.1}$MnO$_3$ have been collected previously by Podobedov et al. The sharp peaks at the top of the wide band are located at 243, 493, and 609 cm$^{-1}$. The high frequency $B_{1g}$ mode at 609 cm$^{-1}$ is suggested as a stretching Mn-O vibration. Recent high pressure studies show that this stretching mode is the most sensitive to pressure with an initial pressure coefficient, $d \ln \nu/dP = 0.01$ GPa$^{-1}$. Thus $d \ln \nu/d \epsilon = 4.4$. Equation (6) gives $d \ln E_P/d \epsilon = -159$. This follows that $E_P$ decreases with increasing compressive strain. This is in good agreement with our experimental fitting parameters as shown in Fig. 5. Combining Eqs. (3) and (6) we can conclude that the strain dependence of $T_c$ mainly results from the strain dependence of the polaronic formation energy though there are also contributions from the electronic bandwidth $W$ and the characteristic phonon frequency $\nu$.

IV. CONCLUSIONS

We have epitaxially grown La$_{0.9}$Sr$_{0.1}$MnO$_3$ thin films on SrTiO$_3$ substrates. The high-temperature resistivity of the films with various thicknesses obeys the small-polaron hopping conductivity in the adiabatic limit. We experimentally find that the small polaronic formation energy $E_P$ decreases with the reduction of the film thickness, which mainly accounts for the the strain effect on $T_c$. By theoretical analysis, we found the contribution from electronic bandwidth is much smaller than that from electron-phonon interaction. We therefore concluded that the electron-phonon coupling is responsible for the strain effect on the high-temperature electronic transport and the ferromagnetic transition temperature in our films.

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