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Oxygen-deficiency-activated anomalous transport in $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films deposited by laser ablation

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Abstract

The transport in oxygen-deficient polycrystalline $La_{2/3}Sr_{1/3}MnO_{3-\delta}$ thin films deposited on Si(111) substrates using laser ablation is studied by measuring the resistivity and ac magnetic susceptibility over the range 2–300 K. The oxygen deficiency results in a serious shift of the insulating–metal (IM) transition toward the low-temperature side and anomalous transport behaviour over the low-temperature range. The ac susceptibility measurement reveals that, upon cooling, the sample exhibits a ferromagnetic transition, a weak anomaly at the IM transition and an antiferromagnetic (AFM) transition which may mainly arise from the charge ordering. Partial melting of the AFM state under a low magnetic field of 750 Oe is observed at 4.2 K.

1. Introduction

The problem of oxygen deficiency in doped manganite perovskites such as $Ln_{1-x}A_xMnO_3$, with Ln standing for the rare-earth elements and A standing for the divalent alkaline-earth elements, has recently received particular attention, primarily due to the fact that oxygen deficiency changes remarkably the transport and magnetoresistive behaviours of these systems [1–3]. To the authors' knowledge, there are at least three types of phenomenon which are relevant to oxygen deficiency in the doped manganite perovskites. First, introduction of oxygen vacancies results in breakdown and bending of local Mn–O–Mn bond chain and then the conduction bandwidth decreases significantly. Therefore, the sample resistivity

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increases rapidly and the metal–insulator transition shifts towards lower temperature with increasing density of oxygen vacancies. For polycrystalline materials, oxygen deficiency is preferred in grain boundary regions, so these boundaries are more like insulating layers (phases) contributing to the high resistivity. Second, lattice distortions and even phase transitions (e.g. from quasi-cubic to tetragonal and to orthorhombic structure) are observed in oxygen-deficient $La_{1-x}Sr_xMnO_3$ (LSMO) and other compounds. These effects will lead to serious changes in transport and magnetic properties for these materials. Recently, it was observed that oxygen-deficient LSMO thin-film samples showed some features associated with charge-ordering (CO) transitions [3]. It was argued that the Mn–O bond is tensioned and bent due to the existence of a number of oxygen vacancies in the lattice, so the CO transition may be activated once the system is subjected to lower temperature.

For the CO effect, it has been established that when the doping fraction x takes commensurate values, i.e. $x = 1/3$, $1/2$ and $1/3$, the CO transition in many $Ln_{1-x}A_xMnO_3$ oxides, such as $Pr_{1-x}Ca_xMnO_3$, $Nd_{1-x}Sr_xMnO_3$ and $Sm_{1-x}Sr_xMnO_3$, is readily observed below a temperature T_{CO} which is quite a lot lower than the ferromagnetic (FM) transition temperature T_c and the insulating–metal (IM) transition temperature T_m. The CO transition is characterized in the lattice configuration by alternating alignments of Mn^{3+} and Mn^{4+} along the c-axis of the orthorhombic lattice. The antiferromagnetic (AFM) alignment is achieved by the coupling of the collinear homovalent Mn spins. Therefore, the CO state, in relation to transport properties, shows a jump of the resistivity by up to several orders of magnitude and an AFM transition at around T_{CO}. A thermal hysteresis depending on the heating and cooling cycle accompanies the CO transition, but the CO state can be made to collapse by application of an external dc magnetic field or dc electric field [5]. These phenomena were confirmed with our previous experiments, although the evidence may not be so direct [4]. It is understood that a narrow one-electron bandwidth W, commonly characterized by a small average ionic radius of the A site $\langle r_A \rangle$ or low tolerance parameter f, achieved through expansion of the Mn–O bond length and/or bending of the Mn–O–Mn bond is generally required for the CO transition [6, 7]. However, the CO transition is hardly observed in LSMO ($x = 1/3$), since $\langle r_A \rangle = 0.124$ nm and $f = 0.975$ for LSMO so large that a large W is established. Stoichiometric LSMO exhibits FM order over a wide temperature range (above room temperature) [5].

In this paper, we present some new experimental data displaying the anomalous transport in oxygen-deficient LSMO polycrystalline thin-film samples. We study the transport properties by measuring the ac magnetic susceptibility, because of its high sensitivity. The operating temperature will be extended down to as low as 2 K. Furthermore, a magnetic field of 5.5 T is used for melting the observed low-temperature AFM state so that distinct differences in melting behaviour can be established. On the basis of a detailed discussion of the various effects of the oxygen deficiency, we shall argue that the anomalous transport behaviour observed in our samples may mainly arises from the CO transition, although other structure inhomogeneities may partially contribute to the anomalous behaviour too.

2. Experimental method

The LSMO films were deposited on Si(111) by pulsed laser deposition using a Lambda Physik KrF excimer laser operating at 248 nm with a pulse width of 30 ns, a repetition rate of 5 Hz and an energy density of about 2 J cm^{-2}. The substrate temperature of 750 °C and oxygen ambient pressure of 10 Pa were kept constant during the deposition. The motivation for choosing 10 Pa—rather than the lower pressure that we previously chose—is the desire to separate the observed AFM transition clearly from the IM or FM transition. A detailed description of the sample preparation was reported earlier [8, 9]. The structure and orientation of the thin films

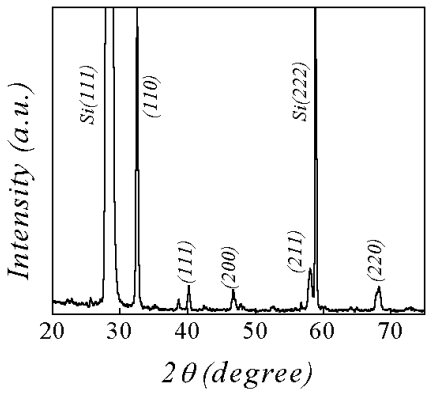

Figure 1. An x-ray θ–2θ scan pattern of the LSMO thin film deposited on Si(111) at low oxygen pressure, showing a (110) textured perovskite structure.

were characterized by means of x-ray diffraction (XRD). The resistance and magnetization were measured using a standard four-pad circuit and an Oxford superconducting vibrating-sample magnetometer (VSM). Measurement of the ac magnetic susceptibility, with and without a dc magnetic field bias, was carried out from 2 K to room temperature. The magnetic field H applied parallel to the thin-film surface was varied between 0 and 5.5 T.

3. Results and discussion

3.1. Transport behaviour

Figure 1 shows a typical XRD pattern of the sample. The film is well crystallized and exhibits perovskite-type structure preferred with (110) orientation. No distinct peak shift as compared to the pattern for the stoichiometric ceramic sample can be found. This indicates that the density of oxygen vacancies in the sample is not high enough to change the lattice stability. Furthermore, no additional peak in the stoichiometric and single-phase XRD spectrum is identified, indicating that there is not much of the second phase produced in the phase separation sequence, within the XRD resolution. The sample resistances R at zero field and $H = 5.5$ T as functions of temperature T are shown in figure 2(a), where curve (c), for the post-annealed sample, is given for reference. At zero field, with decreasing T, the sample resistance exhibits a peak at $T = T_m \sim 72$ K, which corresponds to the IM transition. Further reduction of T results in the resistance rising again; this starts at around $T = 20$ K, and probably indicates an AFM transition. A precise determination of the transition point is not possible from just the R–T curve. At $H = 5.5$ T, there is a marked drop in the resistance throughout the low-temperature range, and the resistance peak becomes lower and shifts to a higher temperature near 175 K. This indicates that the high-resistance state (the AFM state, to be detailed below) has been melted, although the low-temperature tail still indicates high resistance. Such melting results in a big magnetoresistance effect. The as-evaluated magnetoresistance $\mathrm{MR} = [R(0) - R(H)]/R(0)$ as a function of T is presented in figure 2(b). Over the temperature range up to 150 K, a MR value of 80% is recorded. As T rises to 200 from 150 K, the MR value falls to ∼40%. It will be shown below that in between 200 and 150 K, the sample undergoes the FM transition. This MR value would then be maximal. Therefore, the anomalous behaviour at low temperature results in significant enhancement of the MR effect.

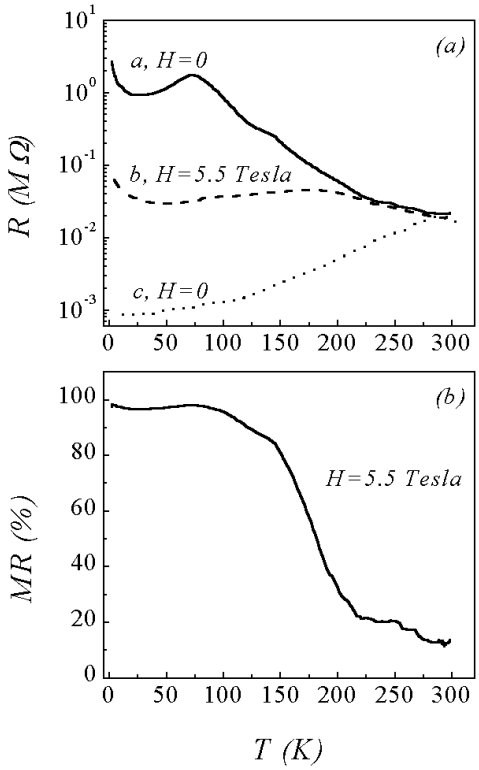

Figure 2. (*a*) The temperature dependence of the resistance for the as-prepared LSMO thin film at zero field (curve (a)), and that at $H = 5.5$ T (curve (b)), plus that for the annealed LSMO thin film at zero field (curve (c)). (*b*) The MR value at $H = 5.5$ T as a function of temperature for the as-prepared LSMO thin film.

3.2. Magnetic susceptibility

Our measurement shows that the anomalous transport of the sample may mainly arise from the CO transition, although we cannot exclude the possibility of other effects, such as lattice distortion and phase separation due to the oxygen deficiency, having an impact. A thermal hysteresis is also observed in the heating-and-cooling-cycle sequence, as reported earlier [4]. Some more direct evidence comes from our ac susceptibility data as a function of T, as shown in figure 3, where the R–T curve is inserted for reference. The dc field bias used for the susceptibility measurement is 250 Oe and the ac frequency is 3250 Hz. The data show clearly the FM transition, identified with the broad peak of χ at $T_c \sim 175$ K (arrow a). Subsequently, an anomaly in the $\chi \sim T$ curve around $T \sim 73$ K, corresponding to the broad IM transition peaked at $T_m \sim 72$ K (arrow b). The big difference ($\sim$100 K) between T_c and T_m indicates that the IM transition in the oxygen-deficient samples is seriously suppressed. A qualitative explanation of this effect can be given on the basis of a picture wherein the double exchange cannot be operated unless the temperature is much lower than T_c, although an alignment of the Mn^{3+}/Mn^{4+} orbit spins has been established at $T \sim T_c$. When $T \sim T_m$, an anomalous fluctuation of χ is observed due to the double exchange.

Upon further cooling, the sample resistance shows a rapid rise; however, $\chi \sim T$ does not exhibit much fluctuation until $T \sim 5.4$ K, at which a jump of χ is observed (arrow c), which

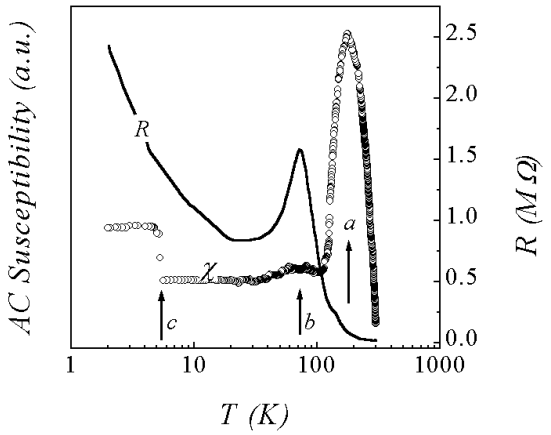

Figure 3. The temperature dependence of the ac magnetic susceptibility χ for the as-prepared LSMO thin film. The susceptibility was measured at 3250 Hz and 0.025 T. The zero-field resistance as a function of temperature is inserted for reference.

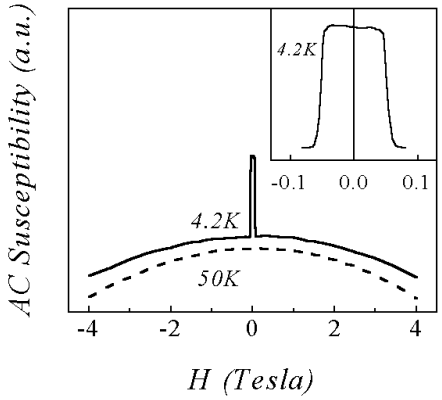

Figure 4. The ac magnetic susceptibility χ for the as-prepared LSMO thin film at 3250 Hz as a function of the biased magnetic field, at the temperatures of 4.2 and 50 K.

obviously characterizes the AFM transition. What is surprising here is that the susceptibility χ jumps from a lower value to a higher one, which is opposite to the behaviour commonly observed at the AFM transition, where χ jumps down from a non-zero value to zero. We have yet to achieve an understanding of this strange behaviour. However, the susceptibility was measured under a biased field of 250 Oe, which is small but seems to have a significant influence on the measured susceptibility.

The AFM phase does not show high stability against magnetic field and can be partially melted even with a low biased magnetic field. Figure 4 shows χ as a function of H at two different temperatures. At $T \sim 50$ K, χ decays smoothly with H. However, the data measured at $T \sim 4.2$ K are quite different. The susceptibility shows a rapid downward jump at $H \sim \pm 750$ Oe, indicating partial melting of the AFM phase. Further increasing of H results in a smooth decay of χ, as in the case at $T \sim 50$ K. This suggests, on the other hand, that the low-temperature phase may be in an AFM state.

3.3. Discussion

We have postulated that the observed low-T anomalous transport behaviour originates from the CO transition. However, the CO transition may not be the sole explanation for this anomalous behaviour. Some effects produced by the oxygen deficiency have been described in section 1. We believe that these effects may contribute to the shift of the metal–insulator transition and the increase of the resistivity. First, we understand that for thin-film samples the strain induced by the mismatch between the underlying substrate and thin film may play a very large role in controlling the transport property, as has been well demonstrated in earlier studies, such as that of Jin *et al* [10]. We prepare our thin-film samples on Si wafers in order to avoid as much as possible the strain effect arising from the mismatch. Also, our samples are quite thick, so the strain in the thin film—if any—near the substrate/film interface should not affect the sample properties much. In fact, substantial strain in thin films would destabilize the CO state [4]. Secondly, oxygen deficiency in epitaxial thin-film samples has been proven to change the metal–insulator transition point and damage the sample conductivity [11–13]. However, the metal–insulator behaviour persists and the low-temperature transport is of metallic type. Therefore, the deficiency-induced lattice inhomogeneity alone cannot explain the AFM transition at low temperature. Thirdly, when the sample is polycrystalline, the oxygen element 'prefers' to evaporate from the grain boundaries. For the case of serious deficiency, the local regions covering grain boundaries may become insulating. Similarly, this should not result in an AFM transition above low temperature.

Another effect that needs to be considered is the phase separation induced by oxygen deficiency in the thin films. Phase separation has been observed in some manganite systems, such as $La_{1-x}Ba_xMnO_3$ and $La_{1/3}Sr_{2/3-x}Ba_xMnO_3$ [14,15]. The main reason for this effect is the large mismatch in the systems induced by doping with very small Ba ions. We expect the appearance of a similar mismatch because of the high oxygen vacancy density in our LSMO samples. Nevertheless, perovskite manganite oxides can stand serious oxygen deficiency with the lattice configuration remaining unchanged. On the other hand, additional peaks should be observable in the XRD spectrum if phase separation occurs. Therefore, we may argue that the anomalous transport behaviour in our oxygen-deficient thin films mainly originates from the CO transition above low temperature. We define $T \sim 5.4$ K as the CO transition point T_{CO} at which the jump of χ is observed, and obviously characterizes the AFM transition. Furthermore, considering the polycrystalline nature of the samples, it should be mentioned that possible inter-grain AFM coupling at low T might contribute to the jump of χ against T (figure 3) or H (figure 4). However, such rapid rising of the resistivity against T cannot be reasonably explained by this coupling: the CO/AFM transition remains the only possible explanation.

Even if we ascribe the anomaly in the transport to the CO transition at low T, we could still argue that a rising of the resistance in our samples does not necessarily indicate a CO transition. There may be some pre-dynamic process at $T > T_{CO}$ which is responsible for the rising of the resistance. One might suggest that a number of local CO phase-like 'micro-zones' appear in the samples at $T > T_{CO}$. Once $T \sim T_{CO}$, the CO phase nucleates at these zones and extends outward. This is a picture of a first-order phase transition, supported by the sharp jump of χ, i.e. the AFM transition. Comparing this jump with the high peak related to the FM transition at 175 K, one may argue that the AFM transition does not yield the whole lattice structure. The sample structure may consist of mixed FM and AFM phases, as we guessed earlier but only confirmed for other systems [16, 17].

Finally, we find that the oxygen-deficiency-activated CO transition at low T can be completely suppressed by annihilating the oxygen vacancies in the LSMO thin films.

We annealed the sample at 850 °C under 1 atm of oxygen for 2 h. The measured R–T curve is shown in figure 2 (curve (c)). It is found that the sample shows metallic behaviour over the whole temperature range and the resistance over the low-T range is several orders of magnitude lower than that for the oxygen-deficient sample. The resistance peak shifts upward as the temperature moves towards room temperature. Normal structural and transport properties, the same as those for stoichiometric LSMO, are measured [4]. This provides us with additional evidence that the CO transition in the pre-annealed sample is oxygen-deficiency activated.

4. Conclusions

In conclusion, we have investigated the anomalous transport in LSMO ($x = 1/3$) thin films deposited on Si(111) wafers at low oxygen pressure by laser ablation. The ac magnetic susceptibility measurements have revealed a FM transition, an IM transition and a possible CO transition, upon cooling of the thin films from 300 to 2 K. The susceptibility data together with the transport property evaluation provide us with new clues that the CO transition can be activated, and consequently the magnetoresistance can be enhanced, by introducing oxygen vacancies in the thin films.

Acknowledgments

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