Insulator–metal transition and magnetoresistance of $La_{0.5}Ca_{0.5}MnO_y$ induced by tuning the oxygen content

Y. G. Zhao,[a] W. Cai, J. Zhao, X. P. Zhang, R. Fan, B. S. Cao, and M. H. Zhu
Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China

Tom Wu, S. B. Ogale, S. R. Shinde, and T. Venkatesan
Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742

Q. Y. Tu
Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

T. K. Mandal and J. Gopalakrishnan
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

(Received 7 February 2002; accepted for publication 29 July 2002)

The oxygen content of $La_{0.5}Ca_{0.5}MnO_y$ was tuned by annealing the samples at high temperatures in flowing nitrogen with graphite powder nearby. The reduction of oxygen content has dramatic effect on the electrical transport and magnetic properties. The samples with $y=2.983$, 2.83, and 2.803 show an insulator–metal transition, and an unusual temperature and magnetic-field dependence of the magnetoresistance. The paramagnetic-ferromagnetic transition also shifts to lower temperatures and the antiferromagnetic transition at lower temperature is suppressed. The results are discussed in terms of the effect of oxygen vacancies on the various properties of $La_{0.5}Ca_{0.5}MnO_y$. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1509108]

I. INTRODUCTION

Manganese perovskites $L_{1-x}A_xMnO_3$, where L and A are trivalent lanthanide and divalent alkaline earth ions, have attracted much interest because of their peculiar electrical transport and magnetic properties;[1] especially the property of colossal magnetoresistance (CMR) which is promising for magnetic applications. In these compounds the spin, charge, and lattice are strongly coupled, leading to various property conditions in the phase diagram of $L_{1-x}A_xMnO_3$.[2] It has been shown that the ground state of $La_{1-x}Ca_xMnO_3$ changes from ferromagnetic (FM) to charge ordering antiferromagnetic (AFM) insulator when Ca doping increases above 0.5.[2] The phase boundary compound $La_{0.5}Ca_{0.5}MnO_3$ is therefore of great scientific interest and focus of significant recent research due to its unique status in the phase diagram.[3–13] Upon lowering the temperature, this compound first undergoes a paramagnetic (PM) to FM phase transition at $T_c \approx 225$ K, and then to a charge ordering AFM phase at $T_{co} \approx 155$ K.[2,4,14] The electrical transport and magnetic properties can be changed dramatically by the magnetic field,[15,16] x-ray irradiation,[17] and Mn site doping with 1% Cr.[18,19] In our previous work,[20] it was shown that the oxygen content has dramatic effect on the electrical transport and magnetic properties of $La_{0.5}Ca_{0.5}MnO_y$ and that the sample with $y=2.83$ shows an insulator–metal transition, with suppression of the AFM transition. It is of interest to explore whether the insulator–metal transition also occurs for samples with other values of oxygen content, and to study the temperature and magnetic-field dependence of the magnetoresistance for $La_{0.5}Ca_{0.5}MnO_y$ samples which show the insulator–metal transition.

In this article, we report a systematic study of the electrical transport and magnetic properties of $La_{0.5}Ca_{0.5}MnO_y$ which show an insulator–metal transition, which occurs for samples with $y=2.983$, 2.83, and 2.803. We have also studied the temperature and magnetic field dependence of the magnetoresistance (MR) for these samples, and have found that the behavior is quite different from those of polycrystalline CMR samples. Decreasing oxygen content also makes the paramagnetic-ferromagnetic transition shift to lower temperatures, and suppresses the AFM transition at lower temperature. The results are discussed in terms of the effect of oxygen vacancies on the properties of $La_{0.5}Ca_{0.5}MnO_y$.

II. EXPERIMENT

The $La_{0.5}Ca_{0.5}MnO_3$ samples were prepared by the standard solid state reaction method using high purity La_2O_3, $CaCO_3$, and MnO_2 powders with appropriate atomic ratio. The mixed powder was ground and calcined at 1050 and 1200 °C several times. The calcined powders were then pressed into pellets and sintered at 1300 °C for 8 h in air followed by slow cooling. In order to reduce the oxygen content of the samples, we annealed the samples at high temperatures for 10 h in flowing N_2 with graphite powder placed near the samples. The oxygen contents of the samples were measured by the titration method, and the oxygen content was found to be reproducible within ± 0.005 per formula unit. We synthesized and examined several such $La_{0.5}Ca_{0.5}MnO_y$ samples with different oxygen contents. We

[a]Also at School of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China; electronic mail: ygzhao@tsinghua.edu.cn

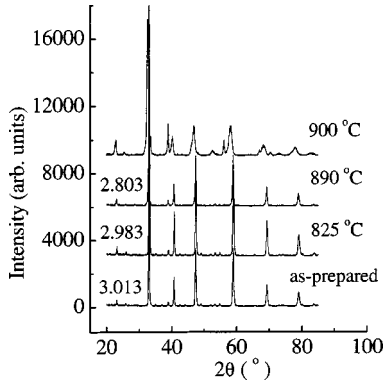

FIG. 1. X-ray diffraction patterns of the as-prepared $La_{0.5}Ca_{0.5}MnO_y$ sample and samples annealed at different temperatures.

note that for the as-prepared sample without oxygen reduction, the oxygen content was found to be $y=3.013$.

The phase analysis of all the samples was performed using a Rigaku D/max-RB x-ray diffractometer with Cu K_α radiation. The electrical resistivity was measured by the four probe method. A superconducting quantum interference device magnetometer was used to measure the temperature dependence of magnetization with the magnetic field parallel to the sample surface. The MR was measured from room temperature to 4 K with the magnetic field in the range of 0–1.2 T.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of the as-prepared $La_{0.5}Ca_{0.5}MnO_y$ sample, and the samples annealed at different temperatures. The x-ray diffraction pattern of the samples annealed below 890 °C is similar to that of the as-prepared sample, indicating that no structure change occurs, although the oxygen content of the annealed samples is reduced remarkably as shown below. However, the x-ray diffraction pattern of the 900 °C annealed sample shows dramatic change as compared to that of the as-prepared sample, suggesting that a structure change or decomposition of $La_{0.5}Ca_{0.5}MnO_y$ occurred due to the over-reduction of the oxygen content. The oxygen contents for the as-prepared sample, 825 °C annealed and 890 °C annealed samples are 3.013, 2.983, and 2.803, respectively. For 900 °C annealed sample, the determination of the oxygen content is a problem due to the possible decomposition, so we denote the oxygen content of this sample as $y<2.083$. Figure 2 shows the variation of the lattice parameters with oxygen content for $La_{0.5}Ca_{0.5}MnO_y$. It can be seen that the lattice parameters do not show monotonic change with oxygen content.

Figure 3 shows the temperature dependence of resistivity for the $La_{0.5}Ca_{0.5}MnO_y$ samples with different oxygen contents. The curve of the as-prepared sample is similar to that reported in the literature,[12] which indicates that the sintering temperature or the grain size influences both the electrical transport and magnetic properties of $La_{0.5}Ca_{0.5}MnO_3$. The insulator–metal transition occurs for the $y=2.983$, 2.830, and 2.803 samples, with the transition temperature around 131, 175, and 120 K, respectively. The transition temperature

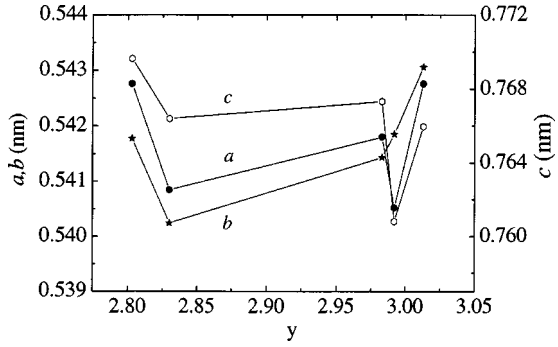

FIG. 2. Variation of the lattice parameters *a,b,c* with oxygen content for $La_{0.5}Ca_{0.5}MnO_y$.

(T_{I-M}) was defined by the peak value of the resistivity. Table I shows the values of T_{I-M} and resistivity at room temperature. It can be seen that the room temperature resistivity increases with the decrease of the oxygen content. The resistivity of sample with $y=2.992$ shows a shoulder at 170 K due to the reduction of the oxygen content. This may indicate that the phase, which shows $I-M$ transition, nucleates in the matrix of the original phase, and coexists with the matrix. The sample with $y=2.830$ has the highest T_{I-M}, so its resistivity at low temperatures is smaller than that of both the $y=2.983$ and $y=2.803$ samples.

In Fig. 4 is shown the temperature dependence of the magnetization for $La_{0.5}Ca_{0.5}MnO_y$ samples with different oxygen contents. The behavior of the as-prepared sample is consistent with that reported in the literature.[12] With the decrease of the oxygen content, the paramagnetic-ferromagnetic temperature (T_c) shifts to lower temperatures and the transition from ferromagnetic to antiferromagnetic (T_N), indicated by the drop of magnetization, is also suppressed. We define T_c as the midpoint of the transition from paramagnetic to ferromagnetic state, and T_N as the midpoint of the transition from ferromagnetic to the antiferromagnetic state. Table I shows the values of T_c and T_N for $La_{0.5}Ca_{0.5}MnO_y$ with different oxygen contents. For the $y=2.983$ sample, it seems that there are two transitions at 230 and 159 K. This two-transition behavior reflects the existence of the mixed phases in samples with small reduction of the oxygen content, as also seen from the resistivity data for the $y=2.992$ sample. The behavior of the 900 °C annealed

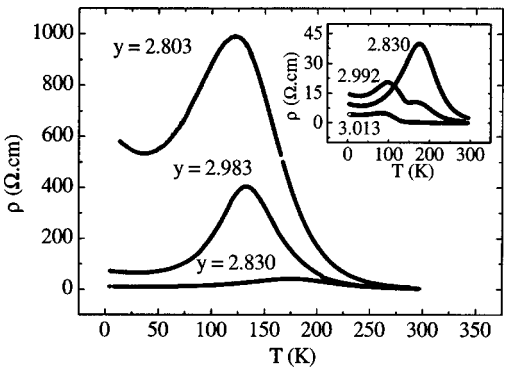

FIG. 3. Temperature dependence of resistivity for $La_{0.5}Ca_{0.5}MnO_y$ samples with different oxygen contents.

TABLE I. The insulator–metal transition temperature (T_{I-M}), paramagnetic to ferromagnetic transition temperature (T_c), ferromagnetic to antiferromagnetic transition temperature (T_N), and the resistivity at 285 K for $La_{0.5}Ca_{0.5}MnO_y$ samples with different oxygen contents (y).

y	T_{I-M} (K)	T_c (K)	T_N (K)	ρ(285 K) (Ω cm)
3.013		231	175	0.025
2.992		231	175	0.775
2.983	131	230, 159		2.763
2.830	175	178		3.257
2.803	120	178		7.180

sample (denoted as $y<2.083$) is different from other samples, and may be complicated due to the structure change and/or multiphase nature. It should be noted that below the paramagnetic to ferromagnetic transition temperature, the magnetization for the $y=2.983$, 2.830, and 2.803 samples shows small decrease with the decrease of temperature. This behavior is different from that of pure ferromagnetic materials and may be related to the existence of the antiferromagnetic phase.

Figure 5 shows the MR data for $La_{0.5}Ca_{0.5}MnO_y$ samples which show the insulator–metal transition. The sample with $y=2.983$ shows MR below 260 K, and a maximum negative MR of ~38% is reached at 160 K in a magnetic field of 12 000 G. The field dependence of MR changes distinctly across 160 K, indicating a crossover. The temperature dependence of MR at moderate fields is nonmonotonic. The sample with $y=2.830$ shows MR below 300 K and maximum negative MR of ~22% is reached at 130 K in a magnetic field of 12 000 G. Once again, a crossover is seen at about the same temperature of 160 K in the field dependence, and a nonmonotonicity in temperature dependence at moderate fields. For the sample with $y=2.803$, the MR increases nearly linearly with magnetic field above 80 K, but shows nonlinearity below 80 K. A negative MR of ~55% is reached at 4.5 K in a magnetic field of 12 000 G. The MR dependence on temperature for this case is monotonic at all fields examined.

Oxygen content reduction in $La_{0.5}Ca_{0.5}MnO_y$ is expected to cause two effects. One is the decrease in the Mn^{4+}/Mn^{3+} ratio, driving the system into the CMR region since $La_{0.5}Ca_{0.5}MnO_3$ is a phase boundary compound, and causing an increase of the room temperature resistivity. It has been shown that the room temperature resistivity of $La_{1-x}Ca_xMnO_3$ decreases with x.[1] Another effect is introducing oxygen vacancies in the Mn–O network, which is important for electrical conduction, resulting in the local distortions in the structure. This structural distortion is also expected to increase the resistivity. These two effects lead to the increase of resistivity of the samples and entrance into the CMR region. Oxygen vacancies in the structure could also change the magnetic interactions, thus affecting the magnetic properties of the samples. The results imply that oxygen vacancies suppress the CO–AFM state. It should be mentioned that for sample with $y=2.983$, the ratio of $Mn^{3+}/(Mn^{4+}+Mn^{3+})$ is close to 54%, comparable to that of $La_{0.54}Ca_{0.46}MnO_3$. From the known bulk phase diagram of $La_{1-x}Ca_xMnO_3$,[2] such a system should show an insulator–metal transition as well as a paramagnetic to ferromagnetic transition around the same temperature of 240 K. This is clearly not observed to be the case in the $y=2.983$ sample. In this case, although the magnetic transition is still close to 240 K, the insulator–metal transition is at ~135 K. For the $y=2.83$ sample, the ratio of $Mn^{3+}/(Mn^{4+}+Mn^{3+})$ is close to 84%, comparable to that of $La_{0.84}Ca_{0.16}MnO_3$, which is a ferromagnetic insulator. This again is in clear contrast to the observed electrical transport and magnetic properties of $La_{0.5}Ca_{0.5}MnO_{2.83}$, which shows an insulator–metal transition and a paramagnetic to ferromagnetic transition around 175 K. This implies that besides the $Mn^{3+}/(Mn^{4+}+Mn^{3+})$ ratio, other factors, such as the

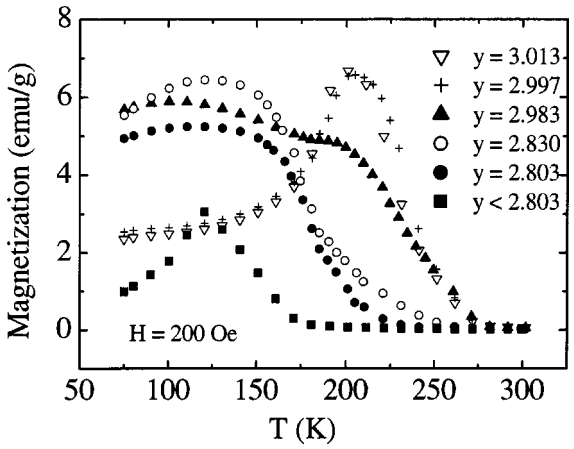

FIG. 4. Temperature dependence of magnetization for $La_{0.5}Ca_{0.5}MnO_y$ samples with different oxygen contents.

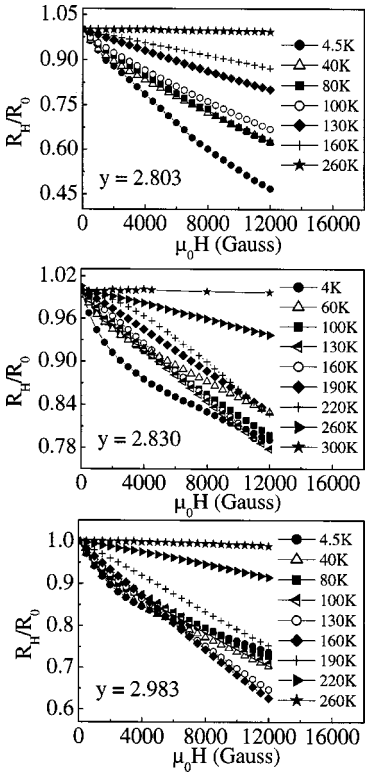

FIG. 5. Magnetoresistance for $La_{0.5}Ca_{0.5}MnO_y$ samples showing the insulator–metal transition.

electron-phonon interaction and spin interaction also play a role in determining the various properties of $La_{0.5}Ca_{0.5}MnO_y$. It should be mentioned that the resistivity and magnetization of our samples do not follow the correlation between resistivity and magnetization shown by Hundley *et al.* on $La_{0.7}Ca_{0.3}MnO_3$ thin films, in that $\rho(H,T)$ is proportional to $\exp[-M(H,T)/M_0]$,[21] where $\rho(H,T)$ and $M(H,T)$ are resistivity and magnetization, respectively.

It has been shown that the MR in the polycrystalline CMR samples exhibits two distinct regions: large MR at low fields dominated by spin-polarized tunneling between grains, and high field MR which is related to the intragrain transport and changes linearly with magnetic field.[22] For the oxygen reduced $La_{0.5}Ca_{0.5}MnO_y$, the temperature and field dependence of MR is quite different from that of the polycrystalline CMR samples. This may be due to the oxygen content reduction induced distortion in both the intergrain and intragrain regions, and this distortion may hinder or modify the spin-polarized tunneling process and change the MR of both the intergrain and intragrain regions. It is possible that the FM conducting phase may be well separated by the AFM insulating phase for the heavily reduced samples, like $y=2.803$ and the MR due to the spin-polarization tunneling vanishes, thereby causing a one slope behavior as observed. Another feature for the MR of the polycrystalline CMR materials is that above 0.5 T, the field dependence of MR is temperature independent,[22] in contrast to the behavior of our oxygen reduced $La_{0.5}Ca_{0.5}MnO_y$. This anomaly deserves further study.

Currently, considerable evidence is building in the literature about inhomogeneity in both the CMR and the charge ordered samples.[6,11,23–25] Pairing of charge ordering stripes in $(La,Ca)MnO_3$ was reported by Mori *et al.*[6] Small regions without charge ordering were also found in the samples[4] and these regions may be related to the ferromagnetic metallic clusters. Uehara *et al.*[23] systematically studied the $La_{5/8-z}Pr_zCa_{3/8}MnO_3$ compounds and their results showed that these compounds are electronically phase separated into submicrometer-scale mixture of insulating regions (with a particular type of charge ordering) and metallic, ferromagnetic domains. Very recently, it was shown that the CMR effect can also be explained by the phase separation model.[26] Phase separation is a clearly possibility in the oxygen reduced $La_{0.5}Ca_{0.5}MnO_y$ samples, as implied by the magnetization results.

IV. SUMMARY

We have studied the electrical transport and magnetic properties of $La_{0.5}Ca_{0.5}MnO_y$ with different oxygen contents. Insulator–metal transition occurs for some samples, and unusual temperature and magnetic field dependence of the MR is observed. The paramagnetic-ferromagnetic transition also shifts to lower temperatures and the AFM transition at lower temperature is suppressed due to oxygen content reduction. The results are discussed in terms of the effect of oxygen vacancies on the various properties of $La_{0.5}Ca_{0.5}MnO_y$. This work shows that the properties of $La_{0.5}Ca_{0.5}MnO_y$ can be changed remarkably by tuning the oxygen content.

ACKNOWLEDGMENT

The work at Maryland was supported under NSF–MRSEC grant No. (DMR-00-80008).

[1] For recent reviews, see *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998); *Colossal Magnetoresistance Oxides*, edited by Y. Tokura (Gordon and Breach, New York, 2000).
[2] P. E. Schiffer, A. P. Ramirez, W. Bao, and S. W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
[3] C. H. Chen and S.-W. Cheong, Phys. Rev. Lett. **76**, 4042 (1996).
[4] P. G. Radaelli, D. E. Cox, M. Marezio, and S.-W. Cheong, Phys. Rev. B **55**, 3015 (1997).
[5] S. Mori, C. H. Chen, and S.-W. Cheong, Phys. Rev. Lett. **81**, 3972 (1998).
[6] S. Mori, C. H. Chen, and S.-W. Cheong, Nature (London) **392**, 473 (1998).
[7] G. Allodi, R. De Renzi, F. Licci, and M. W. Pieper, Phys. Rev. Lett. **81**, 4736 (1998).
[8] G. Kallias, M. Pissas, E. Devlin, A. Simopoulos, and D. Niarchos, Phys. Rev. B **59**, 1272 (1999).
[9] Y. Yoshinari, P. C. Hammel, J. D. Thompson, and S.-W. Cheong, Phys. Rev. B **60**, 9275 (1999).
[10] G. Papavassiliou *et al.*, Phys. Rev. Lett. **84**, 761 (2000).
[11] Q. Huang, J. W. Lynn, R. W. Erwin, A. Santoro, D. C. Dender, V. N. Smolyaninova, K. Ghosh, and R. L. Greene, Phys. Rev. B **61**, 8895 (2000).
[12] P. Levy, F. Parisi, G. Polla, D. Vega, G. Leyva, H. Lanza, R. S. Freitas, and L. Ghivelder, Phys. Rev. B **62**, 6437 (2000).
[13] A. Simopoulos, G. Kallias, E. Devlin, and M. Pissas, Phys. Rev. B **63**, 054403 (2000).
[14] A. P. Ramirez *et al.*, Phys. Rev. Lett. **76**, 3188 (1996).
[15] H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Science **270**, 961 (1995).
[16] Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **74**, 5108 (1995).
[17] V. Kiryukhin, D. Casa, J. P. Hill, B. Keimer, A. Vigliante, Y. Tomioka, and Y. Tokura, Nature (London) **386**, 813 (1997).
[18] A. Barnabe, A. Maignan, M. Hervieu, F. Damay, C. Martin, and B. Raveau, Appl. Phys. Lett. **71**, 3907 (1997).
[19] F. Damay, C. Martin, A. Maignan, M. Hervieu, B. Ravieu, F. Bouree, and G. Andre, Appl. Phys. Lett. **73**, 3772 (1998).
[20] Y. G. Zhao *et al.*, Phys. Rev. B **65**, 144406 (2002).
[21] M. F. Hundley, M. Hawley, R. H. Heffner, Q. X. Jia, J. J. Neumeier, J. Tesmer, J. D. Thompson, and X. D. Wu, Appl. Phys. Lett. **67**, 860 (1995).
[22] H. Y. Huang, S.-W. Cheong, N. P. Ong, and B. Batlogg, Phys. Rev. Lett. **77**, 2041 (1996).
[23] M. Uehara, S. Mori, C. H. Chen, and S. W. Cheong, Nature (London) **399**, 560 (1999).
[24] M. Fath, S. Freisen, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, Science **285**, 1540 (1999).
[25] R. D. Merithew *et al.*, Phys. Rev. Lett. **84**, 3442 (2000).
[26] M. Mayr, A. Moreo, J. A. Verges, J. Arispe, A. Feiguin, and E. Dagotto, Phys. Rev. Lett. **86**, 135 (2001).