View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Marshall University

Marshall University
Marshall Digital Scholar

Physics Faculty Research | Physics

1-1-2002

The effect of phase separation on charge ordering state in La12xCaxMnO3 (x ¼ 1/2, 2/3, and 3/4)

H. D. Zhou

G. Li

S. J. Feng

Y. Liu

T. Qian

See next page for additional authors

Follow this and additional works at: http://mds.marshall.edu/physics_faculty

 Part of the Atomic, Molecular and Optical Physics Commons

Recommended Citation

Zhou, H. -D., Li, G., Feng, S. -J., Liu, Y., Qian, T., Fan, X. -J., & Li, X. -G. (2002). The effect of phase separation on charge ordering state in La1-xCaxMnO3 (x = 1/2, 2/3, and 3/4). Solid State Communications, 122(9), 507-510.

This Article is brought to you for free and open access by the Physics at Marshall Digital Scholar. It has been accepted for inclusion in Physics Faculty Research by an authorized administrator of Marshall Digital Scholar. For more information, please contact zhangj@marshall.edu.

Authors
H. D. Zhou, G. Li, S. J. Feng, Y. Liu, T. Qian, Xiaojuan Fan, and X. G. Li

This article is available at Marshall Digital Scholar: http://mds.marshall.edu/physics_faculty/15

PERGAMON

Solid State Communications 122 (2002) 507–510

solid state communications

www.elsevier.com/locate/ssc

The effect of phase separation on charge ordering state in $La_{1-x}Ca_xMnO_3$ ($x = 1/2$, 2/3, and 3/4)

H.-D. Zhou, G. Li, S.-J. Feng, Y. Liu, T. Qian, X.-J. Fan, X.-G. Li*

Structure Research Laboratory, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China

Received 5 February 2002; accepted 12 March 2002 by H. Akai

Abstract

The magnetic phase separation characteristics are found in manganese perovskite $La_{1/3}Ca_{2/3}MnO_3$ by electron spin resonance (ESR) and magnetization measurements. An extra resonance signal observed in ESR spectra just above the charge ordering (CO) temperature T_{CO} provides strong evidence for the existence of ferromagnetic (FM) clusters near the CO state. The investigation of the resistivity of $La_{1-x}Ca_xMnO_3$ ($x = 1/2$, 2/3, and 3/4) in different magnetic fields up to 14 T shows that the effect of magnetic fields on CO state decreases with increasing x. Our results indicate that the percolative characteristics of the phase separation between FM clusters and CO state for $x = 1/2$ and 2/3 samples are related to the magnetic field dependence of CO state. However, for $x = 3/4$ it is assumed that there are no obvious FM clusters in the CO phase. © 2002 Published by Elsevier Science Ltd.

PACS: 75.30.Kz; 75.30.Vn

Keywords: A. Magnetically ordered materials; D. Electronic transport; D. Phase transitions

1. Introduction

The regime of intermediate and low hole densities of $La_{1-x}Ca_xMnO_3$, the former being close to the antiferromagnetic (AF) CE-type state at $x = 0.5$ and the latter to the AF A-type state at $x = 0$, is complex and interesting. In this region, the ferromagnetic (FM) metallic state caused by double-exchange [1,2] is in competition with other states, notably AF ones, leading to the mixed-phase tendencies. In recent years, a considerable experimental work, such as the electron and X-ray diffraction experiments [3], the study using ^{55}Mn NMR techniques [4], and the analysis of magnetization, resistivity, and specific heat [5,6] has confirmed the existence of mixed-phase of FM and charge ordering (CO) state [7–9] in $La_{1-x}Ca_xMnO_3$ near $x = 0.5$. But whether there is a mixed-phase for $x > 0.5$ is not very clear. Ibarra and De Teresa [10] reported that the $x = 0.65$ state is very stable upon the application of a magnetic field. The studies of Radaelli et al. [11] on the $x = 2/3$ compound arrived at the conclusion that a 'Wigner crystal' charge arrangement is stable at this density. All these results seem to show there is no obvious mixed magnetic phase when $x > 0.5$. In this paper, we used electron spin resonance (ESR) method to detect phase separation in $x = 2/3$ sample for its high sensitivity to the coexistence of different magnetism phases. The coexistence of paramagnetic regime and ferromagnetic regime was observed just above the charge ordering temperature T_{CO}. This intrinsic physical property may be related to the effect of the magnetic field on the CO state.

2. Experimental

Polycrystalline samples of $La_{1-x}Ca_xMnO_3$ ($x = 1/2$, 2/3, and 3/4) were prepared by a standard solid-state reaction method. A stoichiometric mixture of high purity La_2O_3 (baked above 800 °C for 2 h), $CaCO_3$, and MnO_2 was ground and calcined at 1200 °C for 24 h. The reactant was reground intermediately and pressed into pellets for

* Corresponding author. Tel.: +86-551-3603408/3603943; fax: +86-551-3603408.

E-mail address: lixg@ustc.edu.cn (X.G. Li).

0038-1098/02/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0038-1098(02)00148-5

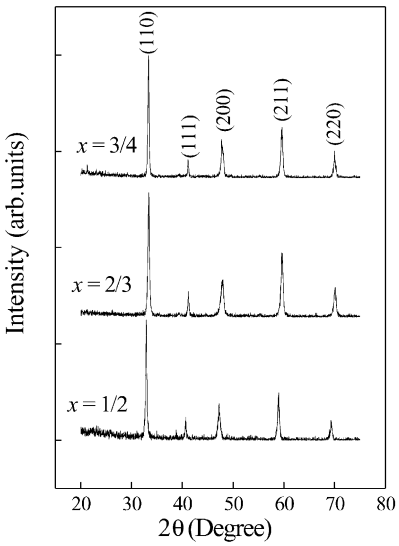

Fig. 1. XRD patterns for the series of $La_{1-x}Ca_xMnO_3$ ($x = 1/2$, 2/3, and 3/4).

sintering at 1300 °C for 24 h. The powder X-ray diffraction patterns were recorded by a MacScience MAXP18AHF diffractometer using Cu Kα radiation. The resistivity was measured by a standard four-probe technique by warming up to the room temperature at a rate of 2 K/min. The ESR measurements were performed at 9.47 GHz using a BRUKER ER-200D spectrometer. The magnetization was measured in a vibrating sample magnetometer (VSM) Ricken Denshi BH55 at a magnetic field of 1000 Oe.

3. Result and discussion

XRD patterns for the series of $La_{1-x}Ca_xMnO_3$ ($x = 1/2$, 2/3, and 3/4) are shown in Fig. 1, and all samples were found to exist in single phase only. The peaks are sharp and can be indexed with the cubic structure.

Fig. 2 shows the temperature dependencies of the resistivity ($\rho(T)$) of $La_{1-x}Ca_xMnO_3$ ($x = 1/2$, 2/3, and 3/4) in different magnetic fields. $\rho(T)$ for $x = 1/2$ (Fig. 2(a)) at zero field rises steeply due to the charge ordering at $T < T_{CO}$ (193 K) which is determined by the peak temperature of the $d \ln \rho(T)/d(1/T) \sim T$ curve in the inset according to Ramirez et al. [12] and when $H = 10$ T it still exhibits semiconductor-like behavior when $T < 123$ K suggesting that the charge lattice does not dissociate. However, it shows metal-like behavior when $H = 12$ and 14 T below 146 K, which implies the collapse of CO state. $\rho(T)$ for $x = 2/3$ (Fig. 2(b)) becomes a bit smaller and exhibits semiconductor-like behavior even as $H = 14$ T, but its T_{CO} obviously shifts to low temperature region with increasing magnetic field as shown in the inset. T_{CO} are equal to 205, 203, 197, and 189 K for $H = 0$, 5, 10 and 14 T, respectively. For $x = 3/4$

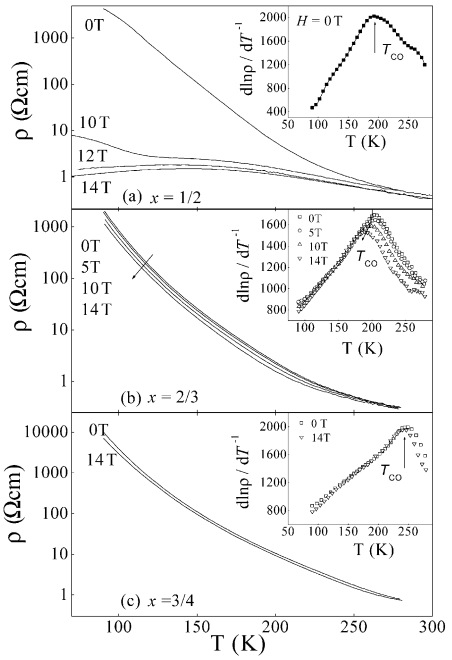

Fig. 2. Temperature dependencies of resistivity in different magnetic fields (Inset: temperature variations of $d \ln \rho(T)/d(1/T)$) for: (a) $La_{1/2}Ca_{1/2}MnO_3$, (b) $La_{1/3}Ca_{2/3}MnO_3$, and (c) $La_{1/4}Ca_{3/4}MnO_3$.

(Fig. 2(c)), T_{CO} (246 K) is almost unchanged even when the magnetic field was up to 14 T.

We replotted the $\rho \sim T$ curves for $La_{1-x}Ca_xMnO_3$ as $\ln(\rho/T) \sim T$ in Fig. 3(a). It is found that the low-temperature resistivity in the CO state in different magnetic fields shows linear dependence quite well, which suggests that the low-temperature resistivity accords with the adiabatic small polaron hopping model, $\rho = BT \exp(E_P/k_BT)$, where B is a constant, E_P the resistivity activation energy, and k_B the Boltzmann constant [13]. Obviously E_P decreases a bit with the increase of H for $x = 2/3$ and 3/4, as shown in Fig. 3(b).

To reveal the magnetic nature of these samples clearly, we measured the ESR spectra of $La_{1/3}Ca_{2/3}MnO_3$ and $La_{1/4}Ca_{3/4}MnO_3$ at various temperatures as shown in Fig. 4(a) and (b), respectively. The ESR signals for $La_{1/3}Ca_{2/3}MnO_3$ consist of a single line which has a line shape close to Lorentzian with Lánder factor $g = 2.0$ above 270 K. This signal is believed to be primarily due to Mn ions in paramagnetic state [14]. Below 270 K, there is an extra peak deviating from the resonance field position with $g = 2.0$ and shifting to low field. At the meantime, the original peak with $g = 2.0$ almost disappears as the temperature decreases to near $T_{CO} = 205$ K as determined from the inset of Fig. 2(b). This result indicates that two different moment phases coexist in this temperature range (270–210 K). As shown in Fig. 5, the magnetization for $La_{1/3}Ca_{2/3}MnO_3$ has a broad shoulder around 210–260 K, which suggests the presence of

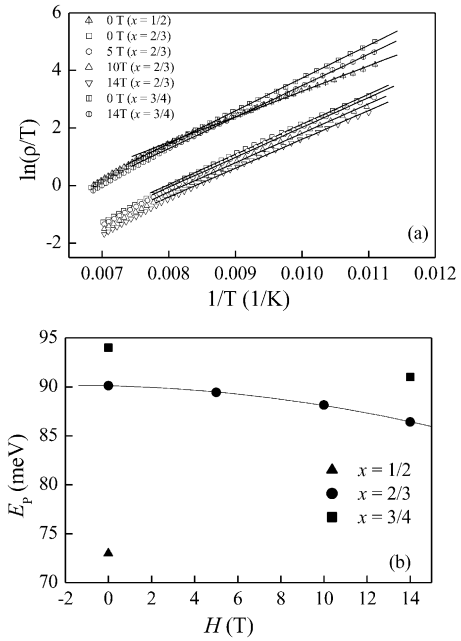

Fig. 3. (a) $\ln(\rho/T)$ versus $1/T$ in different magnetic fields for $La_{1-x}Ca_xMnO_3$. The symbols are experimental data and the solid lines are fits to small polaron model, (b) the magnetic field dependencies of E_P for $La_{1-x}Ca_xMnO_3$. Solid squares are experimental data and the line guides the eyes.

ferromagnetic component in this temperature range. So, the extra line of ESR signal originates from the presence of ferromagnetic phase. This result means that near above CO state there are FM clusters embedded in the paramagnetic background in $La_{1/3}Ca_{2/3}MnO_3$. However, for $La_{1/4}Ca_{3/4}MnO_3$, above $T_{CO} \approx 240$ K the ESR signals of $La_{1/4}Ca_{3/4}MnO_3$ show characteristics of the paramagnetic state and do not have the extra peak. Near T_{CO}, the ESR signals

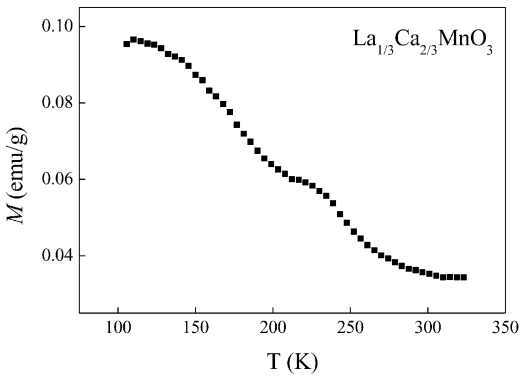

Fig. 5. Temperature dependence of magnetization of $La_{1/3}Ca_{2/3}MnO_3$ under an applied field of 1000 Oe.

change abruptly and the ESR intensity becomes small with the decrease of the temperature due to the appearance of antiferromagnetism [15]. It implies that there is no FM cluster near T_{CO} in $La_{1/4}Ca_{3/4}MnO_3$.

As mentioned earlier, many experiments confirm the mixed-phase FM-CO characteristics near $x = 0.5$. It is proposed that some FM 'islands' persist along with the CO state in $La_{1/2}Ca_{1/2}MnO_3$. The volume fraction of these FM islands, which should be engulfed by the surrounding charge ordered antiferromagnetic bulk, becomes large in an external magnetic field. If the magnetic field is high enough, the volume fraction of the FM islands is so large that these islands can connect each other and so as to generate a ferromagnetic metallic regime in CO/AF state. So when $H = 12$ or 14 T the CO state collapses and exhibits metallic behavior. In $La_{1/3}Ca_{2/3}MnO_3$, the ESR signals show that there are FM clusters near above CO state, which can percolate into CO/AF state and create FM islands with an application of a magnetic field. The volume fraction of FM islands in $x = 2/3$ is not large enough to connect each other

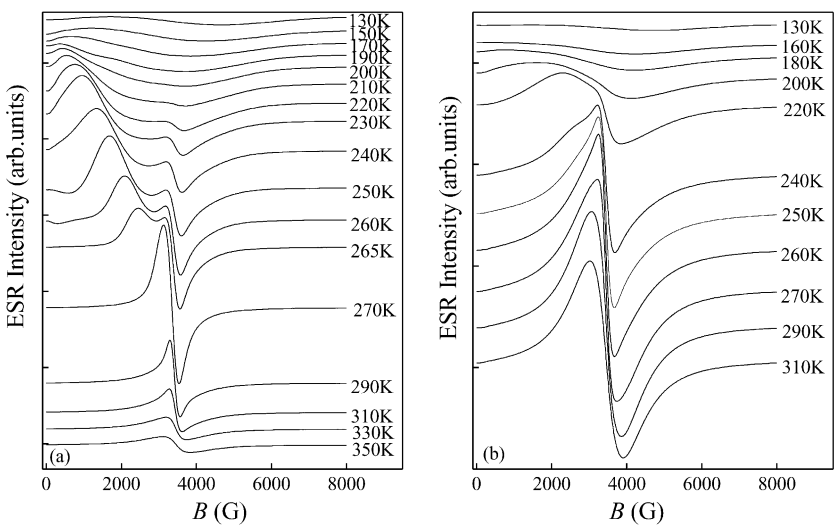

Fig. 4. Temperature evolution of ESR signal of: (a) $La_{1/3}Ca_{2/3}MnO_3$ and (b) $La_{1/4}Ca_{3/4}MnO_3$.

to create metallic regime even when the external magnetic field is up to 14 T. But these FM islands play a role as random fields of the charge and orbital sectors to disconnect the correlation of charge and orbital ordering, and hence induce the delocalization of CO state. With increasing magnetic fields, this effect becomes more obvious as manifested by the decreases in T_{CO} and E_P. In $La_{1/4}Ca_{3/4}MnO_3$, magnetic fields almost do not affect the CO state and the ESR results confirm that there is no PM–FM phase separation, which means that the CO background is very stable and homogeneous.

Acknowledgments

This work was supported by National Natural Science Foundation of China.

References

[1] M. Izumi, Y. Ogimoto, Y. Okimoto, T. Manako, P. Ahmet, K. Nakajima, T. Chikyow, M. Kawasaki, Y. Tokura, Phys. Rev. B 64 (2001) 4429.
[2] C.L. Yuan, Y. Zhu, P.P. Ong, Solid State Commun. 120 (2001) 495.
[3] C.H. Chen, S.W. Cheong, Phys. Rev. Lett. 76 (1996) 4042.
[4] G. Papavassiliou, M. Fardis, M. Belesi, M. Pissas, I. Panagiotopoulous, G. Kallias, D. Niarchos, C. Dimitropoulos, J. Dolinsek, Phys. Rev. B 59 (1999) 6390.
[5] M. Roy, J.F. Mitchell, A.P. Ramirez, P. Schiffer, Phys. Rev. B 58 (1999) 5185.
[6] M. Roy, J.F. Mitchell, P. Schiffer, J. Appl. Phys. 87 (2000) 5831.
[7] A.K. Raychaudhuri, A. Guha, I. Das, R. Rawat, C.N.R. Rao, Solid State Commun. 120 (2001) 303.
[8] Y. Tokura, N. Nagaosa, Science 288 (2000) 462.
[9] R. Kajimoto, H. Yoshizawa, Y. Tomioka, Y. Tokura, Phys. Rev. B 63 (2001) 2407.
[10] M.R. Ibarra, J.M. De Teresa, in: C.N.R. Rao, B. Raveau (Eds.), Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides, World Scientific, Singapore, 1998.
[11] P.G. Radaelli, D.E. Cox, L. Capogna, S.W. Cheong, M. Marezio, Phys. Rev. B 59 (1999) 14440.
[12] A.P. Ramirez, P. Schiffer, S.W. Cheong, C.H. Chen, W. Bao, T.T.M. Palstra, P.L. Gammel, D.J. Bishop, B. Zegarski, Phys. Rev. Lett. 76 (1996) 3188.
[13] N.F. Mott, E.A. Davis, Electronic Processes in Noncrystalline Materials, Clarendon Press, Oxford, 1979.
[14] K.A. Muller, C. Benedek (Eds.), Phase Separation in Cuprate Superconductors, World Scientific, Singapore, 1993.
[15] M. Tovar, G. Alejandro, A. Butera, A. Caneiro, M.T. Causa, F. Prado, R.D. Sanchez, Phys. Rev. B 60 (1999) 10199.