Process dependence of transport properties in phase-separated $Pr_{0.7}Pb_{0.3}MnO_3$ single crystals

Run-Wei Li*
Department of Physics, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße 56, 67663, Kaiserslautern, Germany
International Center for Young Scientists, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305–0044, Japan

Xin Zhou
Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

Bao-Gen Shen
State Key Laboratory of Magnetism, Institute of Physics & Center for Condensed Matter Physics, Chinese Academy of Sciences, P. O. Box 603, Beijing 100080, China

Burkard Hillebrands
Department of Physics, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße 56, 67663, Kaiserslautern, Germany
(Received 6 December 2004; revised manuscript received 27 January 2005; published 30 March 2005)

By means of magnetization, resistance, and electron-spin-resonance measurements at various temperatures it was found that, with increasing temperature, single crystalline $Pr_{0.7}Pb_{0.3}MnO_3$ experiences an unconventional sequence of phase-transition processes, ferromagnetic phase $\rightarrow$ ferromagnetic + paramagnetic phase $\rightarrow$ superparamagnetic + paramagnetic phase $\rightarrow$ paramagnetic phase. Moreover, in the phase-separated temperature range, the metal-insulator transition and the magnetoresistance value are sensitively dependent on the specific processes of temperature change and magnetic field application. On the contrary, the magnetization is process independent. All experimental results can be well understood qualitatively based on a free-energy model considering the distribution of the ferromagnetic phase in the paramagnetic matrix.

DOI: 10.1103/PhysRevB.71.092407 PACS number(s): 75.47.Gk, 75.47.Lx

I. INTRODUCTION

Colossal magnetoresistance (CMR), discovered in ferromagnetic (FM) metallic perovskite manganites $Ln_{1-x}A_xMnO_3$ (Ln=La, Pr, Nd…, A=Ca, Sr, Ba, Pb…), occurs usually accompanied by a metal-insulator transition. The basic microscopic mechanism responsible for this behavior is believed to be the double-exchange interaction, where the hopping of an itinerant e_g electron from the trivalent Mn^{3+} to the tetravalent Mn^{4+} site facilitates both the ferromagnetism and metallic conductivity.[1] In a fully homogeneous double-exchange system, one would expect a sharp metal-insulator transition from the low-temperature metallic FM phase into the high-temperature insulating paramagnetic (PM) phase at the Curie temperature (T_C). However, controversial cases appeared usually in the real samples. Sometimes, the metal-insulator transition temperature (T_{MI}) is lower than T_C, even an FM insulating phase appeared in some samples, which is quite difficult to understand only based on the double-exchange mechanism. There is now compelling experimental evidence that the complex interplay of the electronic degrees of freedom (charge, spin, and orbital) and the lattice leads to a phase separation rather than a single homogeneous phase.[2–12] For example, Uehara *et al.*[13] gave an explanation why the magnetoresistance response increased dramatically when T_C was reduced from the viewpoint of percolative phase separation. By small-angle neutron-scattering experiments, De Teresa *et al.*[14] found for $La_{0.67}Ca_{0.33}MnO_3$ that, when the temperature was slightly above T_C, there were FM metallic clusters imbedded in the PM insulating matrix, and the size of FM clusters changed with increasing temperature and magnetic field. In general, the phase-separation scenario, as an intrinsic feature of perovskite manganites, has been acknowledged gradually. On the other hand, though the appearance of the phase separation in perovskite manganites was verified by various experimental investigations, the evolution process of the magnetic and electric phases with temperature or magnetic field remains an interesting topic.

The competition between the coexisting phases opens the possibility for the appearance of interesting time-dependent effects,[15,16] and even process-dependent effects, which may cause serious influences on physical properties in a phase-separated system.[17,18] More efforts are needed to shed light on the relevance between the configuration of coexisting phases and physical properties. In our previous investigations,[19] it was found that a large low-field magnetoresistance effect appeared in single-crystalline $Pr_{0.7}Pb_{0.3}MnO_3$ when the temperature is slightly above T_{MI}. This result was attributed to spin-dependent electron tunneling between isolated FM clusters. In this article, we focus on the evolution process of the magnetic and electronic phases with temperature and magnetic field. In the single-crystalline $Pr_{0.7}Pb_{0.3}MnO_3$, the phase transition process and its process dependence have been investigated systematically by means of magnetization, transport, and electron-spin-resonance (ESR) measurements. It was found that, with increasing temperature, $Pr_{0.7}Pb_{0.3}MnO_3$ experiences an unconventional phase-transition sequence, FM $\rightarrow$ FM + PM $\rightarrow$ SPM(superparamagnetic) + PM $\rightarrow$ PM. Interestingly, the metal-insulator transition and the obtained CMR values depend intimately on the specific process of temperature

changes and/or magnetic-field applications in the phase-separated temperature region, however, the magnetization is process independent. These results suggest that the specific distribution of the FM phase in this phase-separated system should be a considerably important factor and plays a significant role in transport properties.

II. EXPERIMENTAL DETAILS

Single crystals of $Pr_{0.7}Pb_{0.3}MnO_3$ were grown by the flux-growth method. The growth process and characterization of the structure and composition were described in detail elsewhere.[19,20] Temperature and magnetic-field dependences of the magnetization were measured in a commercial superconducting quantum interference device (SQUID) magnetometer. ESR measurements were carried out at 9.50 GHz using a Bruker-200D spectrometer equipped with a continuous gas-flow cryostat (nitrogen). The ESR spectra were recorded from 200 to 280 K. The dc resistivity was measured using a standard four-probe method. Cu electrodes were prepared by thermal evaporation. The magnetization and resistance were measured in different processes. In process $(5 \rightarrow T, H_0)$, the sample was cooled to 5 K from room temperature without applied magnetic field, then the magnetization/resistance was recorded with increasing temperature under an applied field H_0. In process $(T_0, 0 \rightarrow H)$, the sample was cooled to the desired temperature T_0 without applied magnetic field, then the magnetic-field dependence of the magnetization and/or resistance was recorded at this desired temperature T_0.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows the temperature evolution of the magnetization and resistance. It is clearly indicated that the sample is ferromagnetic and metallic at low temperature, and paramagnetic and insulating when the temperature is above 235 K. Though one would expect a metal-insulator transition to occur at or below T_C in a homogeneous double-exchanged system, it is not the case in our sample. If T_{MI} and T_C are defined as shown in Fig. 1(a), T_{MI} is about 30 K higher than T_C. In other words, it seems that a "metallic PM phase" appears in a narrow temperature region. The inset of Fig. 1(b) indicates ESR spectra measured from 205 to 270 K. When the temperature is above 260 K, the ESR signals consist of a single peak with $g=2.0$ nearly independent of the temperature. This signal has been believed to be due primarily to PM Mn ions.[21,22] When the temperature is below 260 K, which is much higher than the T_C ($\sim$205 K), a nascent FM resonance peak appears at low field. In other words, the FM phase appears when the temperature is below 260 K, though no FM characteristic was detected by SQUID above 220 K [see the inset of Fig. 1(a)]. As shown in Fig. 1(b), the resonance field of the nascent FM phase is almost independent of the temperature below 235 K, which is just T_{MI}. This suggests that the magnetic ordering in the nascent FM phase is rather stable and hardly changes with increasing temperature below the T_{MI}. Increasing the temperature further above T_{MI}, the resonance field of the nascent FM phase begins to increase with temperature and disappears above 260 K.

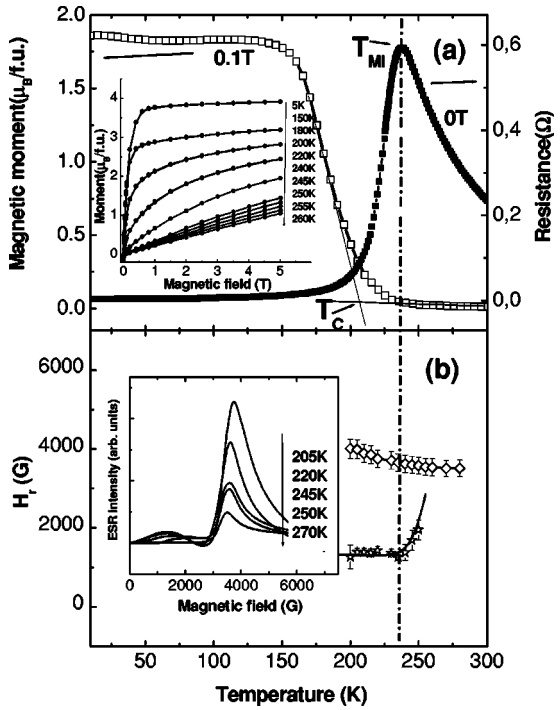

FIG. 1. (a) Temperature dependence of the magnetization (under a field of 0.1 T) and zero-field resistance. The upright dash-dot lines indicate the metal-insulator transition temperature (T_{MI}). The inset of Fig. 1(a) shows the magnetization as a function of the magnetic field at various temperatures. (b) Temperature dependence of the ESR resonance field. The inset of Fig. 1(b) shows ESR spectra measured from 205 to 270 K.

Combining magnetization, resistance, and ESR results, the phase-transition process of $Pr_{0.7}Pb_{0.3}MnO_3$ can be extracted unequivocally. At low temperature, the sample is in a homogeneous FM metallic phase. When the temperature approaches T_C, phase separation occurs. A nascent FM phase with a relatively rich hole concentration separates from the PM matrix. Below T_{MI} (235 K), the FM phase fraction is above the percolation threshold value and the sample exhibits metallic behaviors. The nascent FM ordering is relatively stable so that an increasing temperature only decreases the FM phase fraction, however, destroys hardly the FM ordering. When the temperature is above T_{MI}, the FM fraction is below the percolation threshold value and the connected FM phase is broken into isolated FM clusters and behaves as a superparamagnetic (SPM) state. Consequently, the sample acts as an insulator and no obvious FM characteristics can be observed in the SQUID measurement due to its relatively longer measuring time. An increasing temperature reduces the sizes of these isolated FM clusters and destroys the FM ordering. As a result, the FM phase fraction decreases and the resonance field increases with increasing temperature. In general, with increasing temperature, $Pr_{0.7}Pb_{0.3}MnO_3$ experiences an FM $\rightarrow$ FM + PM $\rightarrow$ SPM + PM $\rightarrow$ PM phase transition sequence.

As shown above, the single-crystalline $Pr_{0.7}Pb_{0.3}MnO_3$ experiences a complex and unconventional phase-transition process with increasing temperature. Such a phase transition should be sensitive to external disturbances, which can cause

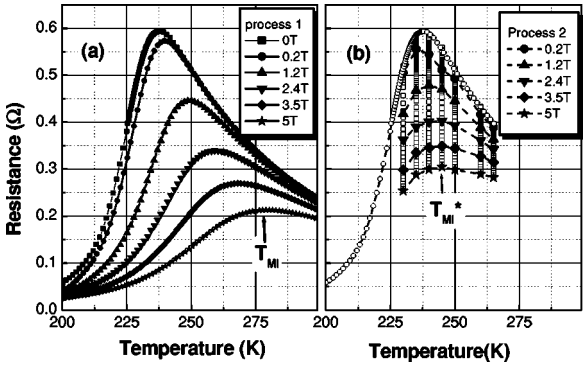

FIG. 2. Resistance as a function of the temperature and the magnetic field in (a) process $(5\rightarrow T,H_0)$ and (b) process $(T_0,0\rightarrow H)$.

probably process-dependent effects in the physical properties. Here, the temperature and magnetic-field dependences of the magnetization and resistance were measured in process $(5\rightarrow T,H_0)$ and $(T_0,0\rightarrow H)$, respectively. Comparing Figs. 2(a) and 2(b), one can find that: (1) the terminal resistance value is quite different in both processes. For example, under a magnetic field of 5 T, the resistance is 0.11 Ω at 245 K in process $(5\rightarrow T,H_0)$, much smaller than in process $(T_0,0\rightarrow H)$ (0.31Ω). In other words, the magnetoresistance values MR ($MR=[R(0)-R(H)/R(0)]\times 100\%$, where $R(0)$ and $R(H)$ are the resistance at absence and presence of field) calculated from the data of process $(5\rightarrow T,H_0)$ and $(T_0,0\rightarrow H)$ are remarkably different. In order to show this point clearly, the MR as a function of temperature and magnetic field is shown in Fig. 3. In general, the MR in process $(5\rightarrow T,H_0)$ is much larger than in process $(T_0,0\rightarrow H)$. For example, at 230 K, a magnetic field of 5 T induces a MR as large as 90% in process $(5\rightarrow T,H_0)$ and only 50% in process $(T_0,0\rightarrow H)$. Under a high magnetic field, the maximum of the MR appears near 235 K in both processes. However, under a lower magnetic field, for example, 0.2*T*, the maximum of the MR appears at 225 K in process $(5\rightarrow T,H_0)$, 10 K lower than T_{MI} under a zero field, and at 245 K in process $(T_0,0\rightarrow H)$. 20 K higher than in process $(5\rightarrow T,H_0)$. The

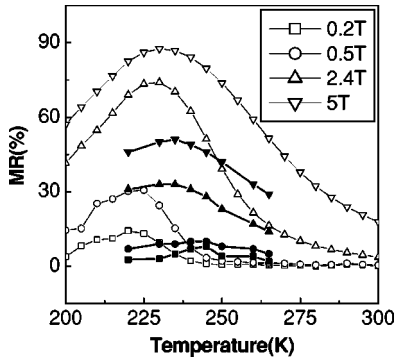

FIG. 3. Temperature dependence of the MR ($MR=[R(0)-R(H)/R(0)]\times 100\%$, where $R(0)$ and $R(H)$ are the resistance at absence and presence of field, measured under various magnetic fields in process $(5\rightarrow T,H_0)$ (hollow symbols) and process $(T_0,0\rightarrow H)$ (solid symbols).

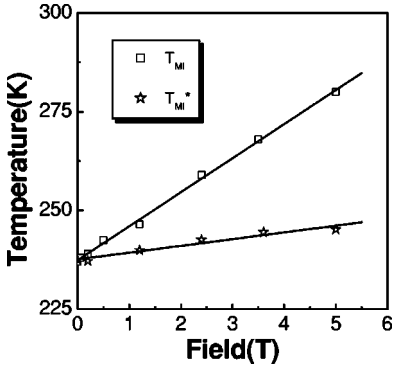

FIG. 4. Magnetic-field dependence of metal-insulator transition temperature in process $(5\rightarrow T,H_0)$ (T_{MI}) and process $(T_0,0\rightarrow H)$ $(T_{\mathrm{MI}*})$.

large MR appearing slightly above T_{MI} in process $(T_0,0\rightarrow H)$ has been attributed to the spin-dependent electron tunneling between isolated FM clusters, which was reported in detail in Ref. 19. Therefore, considering the considerable process dependence, the MR value cannot be extracted strictly from process $(5\rightarrow T,H_0)$. (2) As shown in Fig. 4, T_{MI} increases linearly with magnetic field in process $(5\rightarrow T,H_0)$. The application of magnetic field of 5 T increases T_{MI} from 235 K to 280 K. If we define the peak temperature in resistance-temperature curve in process $(T_0,0\rightarrow H)$ as $T_{\mathrm{MI}*}$ [see Fig. 2(b)], the magnetic field even up to 5 T changes slightly the $T_{\mathrm{MI}*}$. Generally, both the metal-insulator transition and MR value are obviously process dependent.

Completely different from the resistance, the magnetization is independent of the measuring process. As shown in Fig. 5, the magnetization values measured in both processes coincide with each other completely. Considering the different process dependences of the magnetization and resistance, one can conclude that the concentration of the FM phase is independent of the measuring process. However, the distribution of FM clusters in the PM matrix may be affected by the measuring process and plays a critical role on transport properties, i.e., metal-insulator transition and CMR. In the phase-separated temperature range, the system tends to transform from a connected distribution state to an isolated dis-

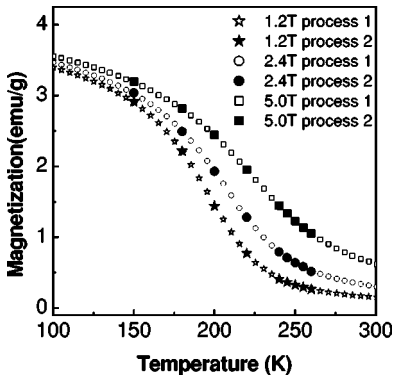

FIG. 5. Magnetization as a function of the temperature and magnetic field in process $(5\rightarrow T,H_0)$ (hollow symbols) and process $(T_0,0\rightarrow H)$ (solid symbols).

tribution state in process $(5 \rightarrow T, H_0)$ while there is a reversal tendency in process $(T_0, 0 \rightarrow H)$. The process dependence of transport properties (or say the distribution of the FM clusters) implies that there exist free-energy barriers between different cluster distribution states, so that the transition between these different distibution states is first order.

As an example, we consider only two kinds of regular distributions of the FM clusters: (i) droplike distribution (isolated FM clusters) and (ii) stripelike distribution (connected FM clusters). The free energy of a unit volume phase-separated system can be written as

$$\Delta f = y f_m + f_s + f_c$$

where y is the volume concentration ratio of the FM phase, f_m is the magnetic free energy of the FM phase, f_s is the interface energy between FM clusters and the PM matrix, and f_c is Coulomb energy intra- and/or inter-FM clusters. In an electronic phase-separated system, the rich-hole FM phase separating from the PM matrix is favorable to lower the magnetic free energy. The interface energy f_s favors to form a single FM phase, while the Coulomb energy f_c tends to break the FM phase into small clusters. As a result, the competition among these energies determines the phase components and their specific distributions.[23] It is known that f_s is proportional to $y^{2/3}/d$ in the droplike distribution state and $y^{1/2}/d$ in the stripelike distribution state, respectively, and f_c is proportional to d^2 only with a small difference in the coefficients in both distribution states aforementioned,[24] where d is the average distance between drops or stripes. Notably, when y is above one certain critical value, the stripelike distribution state is of a smaller interface energy and a comparable Coulomb energy (even with a macroscopic size in one or two dimensions[24]) than the droplike distribution state. Therefore, the transition can occur between the two distribution states. The transition must be accompanied by the deformation of the FM clusters. In other words, the system will experience some transition states with deformed FM clusters, which are of higher interface energy as well as possible Coulomb energy and serve as energy barriers between the droplike and stripelike distribution states. As a result, the transition between different distribution states is first order and causes the process dependence in transport properties.

IV. SUMMARY

We have investigated the temperature evolution of the magnetic and electronic phases and the process dependence of magnetic and transport behaviors in single-crystalline $Pr_{0.7}Pb_{0.3}MnO_3$. It was found that, with increasing temperature, $Pr_{0.7}Pb_{0.3}MnO_3$ experiences an FM $\rightarrow$ FM + PM $\rightarrow$ SPM + PM $\rightarrow$ PM phase-transition sequence. The metal-insulator transition and the MR values are process dependent. A free-energy model considering the distribution of FM clusters has been proposed to understand qualitatively the phase-separation and process dependences of transport properties. In other words, considering only phase separation and usual random percolation may not be sufficient to understand the rich experimental phenomena in perovskite manganites.

ACKNOWLEDGMENTS

R. W. L. and X. Z. would like to thank Alexander von Humboldt Foundation for financial support. The authors would also like to thank Professor Sergej O. Demokritov for his helpful suggestions and discussions.

*Corresponding author. Email: runwei.li@nims.go.jp

[1] C. Zener, Phys. Rev. **82**, 403 (1951).
[2] A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1999).
[3] G. Papavassiliou, M. Fardis, M. Belesi, T. G. Maris, G. Kallias, M. Pissas, D. Niarchos, C. Dimitropoulos, and J. Dolinsek, Phys. Rev. Lett. **84**, 761 (2000).
[4] J. Dho, I. Kim, and S. Lee, Phys. Rev. B **60**, 14 545 (1999).
[5] Y. Yoshinari, P. C. Hammel, J. D. Thomson, and S. W. Cheong, Phys. Rev. B **60**, 9275 (1999).
[6] G. Allodi, R. De Renzi, F. Licci, and M. W. Pieper, Phys. Rev. Lett. **81**, 4736 (1998).
[7] M. Uehara, S. Mori, C. H. Chen, and S-W. Cheong, Nature (London) **399**, 560 (1999).
[8] I. Kim, J. Dho, and S. Lee, Phys. Rev. B **62**, 5674 (2000).
[9] M. Fäth, S. Freisem, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, Science **285**, 1540 (1999).
[10] S. Mori, C. H. Chen, and S-W Cheong, Phys. Rev. Lett. **81**, 3972 (1998).
[11] P. Dai, J. A. Fernandez-Baca, N. Wakabayashi, E. W. Plummer, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **85**, 2553 (2000).
[12] T. Becker, C. Streng, Y. Luo, V. Moshnyaga, B. Damaschke, N. Shannon, and K. Samwer, Phys. Rev. Lett. **89**, 237203 (2002).
[13] M. Uehara, S. Mori, C. H. Chen, and S-W. Cheong, Nature (London) **399**, 560 (1999).
[14] J. M. De Teresa, M. R. Ibarra, P. A. Algarabel, C. Ritter, C. Marquina, J. Blasco, J. Garsia, A. del Moral, and Z. Arnold, Nature (London) **386**, 256 (1997).
[15] N. A. Babushkina, L. M. Belova, D. I. Khomskii, K. I. Kugel, O. Yu. Gorbenko, and A. R. Kaul, Phys. Rev. B **59**, 6994 (1999).
[16] T. Kimura, Y. Tomioka, R. Kumai, Y. Okimoto, and Y. Tokura, Phys. Rev. Lett. **83**, 3940 (1999).
[17] Run-Wei Li, Ji-Rong Sun, Qing-An Li, Zhao-Hua Cheng, Zhi-Hong Wang, Shao-Ying Zhang, and Bao-Gen Shen, J. Phys.: Condens. Matter **13**, 1973 (2001).
[18] Run-Wei Li, Ji-Rong Sun, Zhi-Hong Wang, Xin Chen, Shao-Ying Zhang, and Bao-Gen Shen, Chin. Phys. **9**, 630 (2000).
[19] Run-Wei Li, Zhi-Hong Wang, Wei-Ning Wang, Ji-Rong Sun, Qing-An Li, Shao-Ying Zhang, Zhao-Hua Cheng, Bao-Gen Shen, and Ben-Xi Gu, Appl. Phys. Lett. **80**, 3367 (2002).
[20] Ben-Xi Gu, Shi-Yuan Zhang, and You-Wei Du, Chin. Phys. Lett. **18**, 598 (2001).
[21] A. Shengelaya, G.-M. Zhao, H. Keller, and K. A. Müller, Phys. Rev. Lett. **77**, 5296 (1996).
[22] S. B. Oseroff, M. Torikachvili, J. Singley, S. Ali, S.-W. Cheong, and S. Schultz, Phys. Rev. B **53**, 6521 (1996).
[23] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
[24] Xin Zhou *et al.* (unpublished).