

Critical Parameters and Magnetocaloric Effect of the $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.9750}\text{Pd}_{0.025}\text{O}_3$ Compound

L. V. Bau, N. M. An

Hong Duc University, Thanh Hoa, Vietnam
Email: levietbau@yahoo.com

Received 10 June 2014; revised 15 August 2014; accepted 8 September 2014

Copyright © 2014 by authors and Scientific Research Publishing Inc.
This work is licensed under the Creative Commons Attribution International License (CC BY).
<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

The $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.9750}\text{Pd}_{0.025}\text{O}_3$ compound was studied using DC magnetization measurements. The data were analyzed in the paramagnetic-ferromagnetic phase transition region by the Arrott plot method. The results show the Curie temperature $T_C \sim 247.8$ K and the critical exponents of $\beta = 0.48633$, $\gamma = 1.18623$ and $\delta = 3.431682$. The values of the critical exponents are between the mean-field theory and 3D Ising model. The magnetocaloric value is ~ 5 J/kgK, extracted from the $M(H)$ curves.

Keywords

Magnetocaloric, Critical Parameters, Perovskite

1. Introduction

Above the Curie temperature T_C , colossal magnetoresistance (CMR) perovskite manganites behave paramagnetic insulating state. As the temperature is decreased below T_C , they become ferromagnetic metals. It is shown that the ferromagnetic clusters are formed and extracted as decreasing temperature below T_C . The existence of ferromagnetic clusters above T_C [1] as well as inhomogeneity and phase separation [2] suggests that ferro-magnetic long-range order may be established by percolation of ferromagnetic regions as the temperature is lowered. Such magnetic inhomogeneities in the spin systems may be a result in a reduced local effective topological dimensionality [3], thereby leading to different critical behaviors. Hence, the critical properties of the paramagnetic-ferromagnetic (PM-FM) phase transitions in manganites pose an important fundamental problem. On the other hand, the vast variability of competing mechanisms, which may influence the magnetic ordering, may also yield other types of paramagnetic-ferromagnetic transitions for different systems in this class of materials. Experi-

mental studies [4]-[6] of critical behavior of manganites near the PM-FM phase transition by using a variety of techniques have yielded a wide range of values for the critical exponent of β . The values range from about 0.3 - 0.5, which embrace mean-field ($\beta = 0.5$), three-dimensional (3D) isotropic nearest-neighbor Heisenberg ($\beta = 0.365$) and 3D Ising ($\beta = 0.325$) estimates. Static dc-magnetization measurements [4]-[7], in addition to β , also yield the critical parameters γ and δ for initial susceptibility $\chi(T)$ and critical isotherm $M(T, H)$, respectively. However, they may fail to determine a unique universality class for the phase transition of these manganites. The very low values of $\beta = 0.095$ for LaMnO_3 [5] and 0.147 for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [6] obtained from static magnetization measurements suggest that the PM-FM transition in these compounds is first-order transition. Further, a first-order PM-FM phase transition has been reported [8] for $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ based on the sign of the slope of the isotherm plots, $(H/M)^{1/\gamma}$ vs. $M^{1/\beta}$ ($\gamma = 1$ and $\beta = 0.5$ or $\gamma = 1.336$ and $\beta = 0.365$). Interestingly, a continuous transition has been reported [7] for $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$. Recently, a critical point has been identified [9] in the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ phase diagram at $x = 0.4$, thus marking a boundary between first- and second-order phase transitions. $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, a typical perovskite, has generated much interest in recent work. It has a ferromagnetic transition near 360 K [10], which is the highest T_C among perovskite manganites having the same $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio of 7/3. The critical parameters of manganites materials have been reported in a number of publications. It is interesting that the temperature can be shifted to room temperature for applications.

According to the Curie-Weiss law for ferromagnetism, the large magnetic entropy change, $\Delta S_{M(T,H)}$, is expected at the Curie temperature T_C and has high values for materials having large effective magnetic moment [11]. Since 1996, there have been numerous reports of exceptionally large magnetocaloric effects in perovskite manganese oxides [12]-[16]. In this paper, we report the critical parameters β , γ and δ determined from the Arrott plots, Arrott plots modified and magnetocaloric effects of the $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.975}\text{Pd}_{0.025}\text{O}_3$ compound by analyzing the magnetization curves.

2. Experiments

The sample was fabricated by the sol-gel method. The original chemical substance are $\text{La}(\text{NO}_3)_3$, $\text{Ca}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$ and PdCl_2 with the pure of more than 99.99%. The sample had been heated at 980°C for 3 hours. After that it had been sintered at 1050°C for 4 hours in air. Sample was checked and confirmed by X-ray diffraction. The results show that the sample was quality with structure of orthorhombic. The magnetic measurements were carried out on the PPMS-6000.

3. Results and Discussion

Figure 1 shows the temperature dependence of magnetisation of the sample measured in the applied field of 100 Oe using zero field cooled and field cooled mode. The ferro-paramagnetic transition temperature is $T_C = 252.7$ K, defined from derivative the $M(T)$ curve as temperature. The sample behaves the second-order-phase transition. It also behaves a large of the range of temperature. This is a typical behavior of the samples fabricated by sol-gel

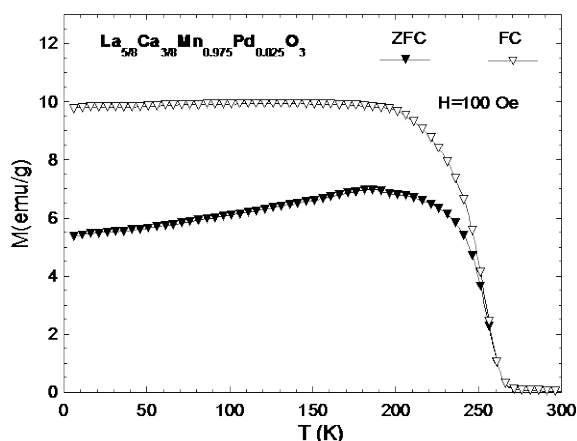


Figure 1. The temperature dependence of the magnetisation of the $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.975}\text{Pd}_{0.025}\text{O}_3$ sample.

method. The range of the wide of transition as well the difference between the zero-field cooled and field cooled in the range of low temperature does not seem to reflect the chemical disorder but seems due to the disorder in magnetism. It may be a result of phase separation phenomenon [15].

Figure 2 shows the magnetic field dependence of magnetization at different temperatures. It can be seen that at low temperatures, far from T_C , the value of magnetisation of the sample is not saturated. To understand clearly the interaction between the samples, we have built the Arrot plots. The transition temperature, of course, is not shown from the shape of the curves even though near the phase transition. So we have had to build the Arrot plots modified by using the critical exponents.

In the range of the ferro-paramagnetic transition temperature, the scaling law was used for the saturate magnetisation and susceptibility and given by [16] [17]. The critical parameters β and γ , are inferred by using $M_S(T) = \lim_{H \rightarrow 0} H$ in the temperatures of $T < T_C$. The susceptibility is defined by the equation $\chi_0^{-1} = \lim_{M \rightarrow 0} \frac{H}{M}$ in the range of temperatures $T > T_C$. At the ferro-magnetic transition temperature, the applied field dependence of the susceptibility is given by $M = D.H^{\frac{1}{\delta}}$, where the critical parameter $\delta = 1 + \gamma/\beta$. The value of δ can be found from the $\log(M)$ curves versus $\log(H)$ at T_C . By the extrapolating the Arrot plots, we have gained the saturate magnetisation and susceptibility as shown in the **Figure 3**. The critical parameters of the sample are defined of $\beta = 0.48633$, $\gamma = 1.1826$ and $\delta = 3.431682$. This implies that both mean-field and Heisenberg model are not applied for those samples. As mentioned above, the samples are complicated phase in physics so this term can be

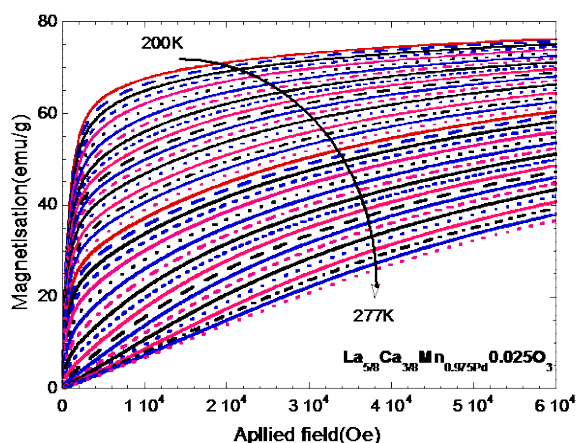


Figure 2. The isotherm curves of the $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.975}\text{Pd}_{0.025}\text{O}_3$ sample at different temperatures.

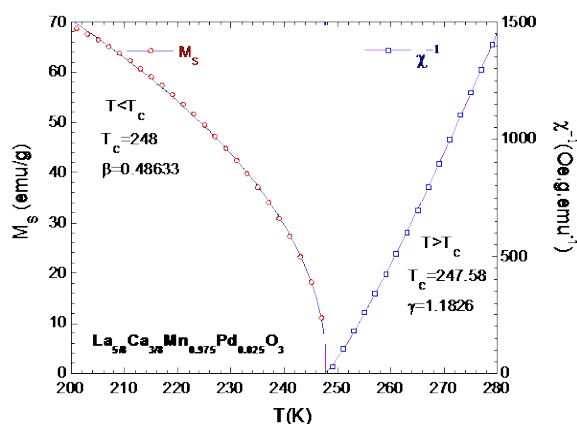


Figure 3. The temperature dependence of the saturate magnetisation and susceptibility of the $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.975}\text{Pd}_{0.025}\text{O}_3$ sample.

explained by a point of view of phase separation. The critical parameters defined are between the mean-field and Heisenberg model. This suggests that the sample seems not to be single phase but at least two phases, which should obey mean-field and Heisenberg model.

The thermo-magnetisation measurements show the transition temperature $T_C = 252.7$ K. However, it is relative based on the derivative of the curve $M(T)$ as T . This value was defined at the peak of the derivative curve. At this temperature, the variety of magnetisation as temperature is the strongest. Based on the obtained results, we have calculated and defined the ferro-magnetic transition temperature of the sample $T_C = 247.79$ K. This is mean value after calculating both temperature regions above and below T_C . It is much different to the value defined by the magnetisation curve. However, this value is more exactly because it is defined in the region of phase transition. It behaves the nature of the transition process in the sample.

The Arrot plots modified were built using the critical parameters. The result is shown in the **Figure 4**. The Arrot plots modified show the difference above the shape of the between two regions, above and below T_C , which was defined to be $T_C = 247.79$ K by analyzing the data of saturate magnetisation and susceptibility. This shows that there is a strongest change of magnetic order of the sample at 247.9 K.

The magnetocaloric phenomena was investigated using the applied field dependence of the magnetisation, $M(H)$, at different temperatures. The result is displayed in the **Figure 5**. The magnetocaloric curves calculated for the applied fields of 0.5 T up to 6.0 T. As can be seen from **Figure 5**, the peaks of those curves shift to the higher temperature in higher applied field. In the low field, magnetocaloric shift to the ferro-paramagnetic transition temperature, $T_C = 247.79$ K. This can be understood that the magnetocaloric phenomenon is strongest at

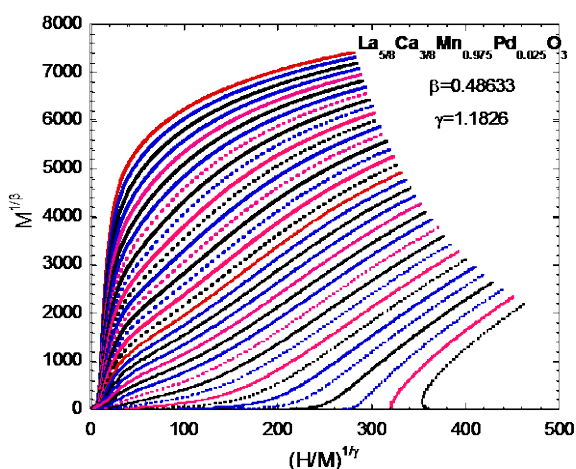


Figure 4. The Arrot modified of $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.975}\text{Pd}_{0.025}\text{O}_3$.

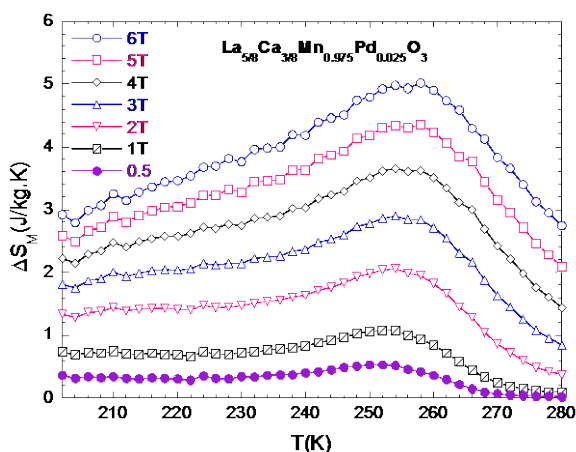


Figure 5. The CME in the $\text{La}_{5/8}\text{Ca}_{3/8}\text{Mn}_{0.975}\text{Pd}_{0.025}\text{O}_3$ sample in the difference applied fields.

the phase transition temperature related to the applied field for the thermo-magnetisation measurements. The shifting of the peaks due to the transition phase temperature is shifted to higher in high applied field. Approximate of 5 J/Kg·K is the maximum value of magnetocaloric gained in the applied field of 6 T. Despite of small but it is close to room temperature. It is interesting that the magnetocaloric phenomenon broad over temperature region. It reduces sharply as increasing temperature higher T_C whereas it reduces more slowly in the temperature lowers T_C . This can be explained that in the temperature higher T_C , the materials is paramagnetic and it is ferromagnetic in the lowers T_C .

Phase separation of the materials can affect the positive effects at T_C such as magnetoresistance or magnetocaloric. For the magnetoresistance, phase separation plays a role in the temperature region. It enhances the low-field magnetoresistance especially in low temperatures, far from T_C . However, the magnetocaloric is not enhanced in low temperatures. This is a challenge for application.

4. Conclusion

The critical parameters have been studied. The results show $\beta = 0.48633$, $\gamma = 1.1826$ and $\delta = 3.431682$. This means that the transition model of the sample is between the mean-field and the Heisenberg mode. The thermo-magnetic properties were investigated. The results show that Pd substituted for Mn in the materials reduces the ferro-paramagnetic transition temperature as well as magnetocaloric. However, the region of temperature having magnetocaloric is broadened to the lower transition temperature.

Acknowledgements

This work was supported by the National Foundation for Science & Technology Developments (NAFOSTED), Vietnam, project code: 103.02-2010.28. We thank Dr. Dao Nguyen Hoai Nam working for Institute of Materials Science of his measurements as well as his comments.

References

- [1] De Teresa, J.M., Ibarra, M.R., Algarabel, P.A., Ritter, C., Marquina, C., Blasco, J., Garcia, J., del Moral, A. and Arnold, Z. (1997) Evidence for Magnetic Polarons in the Magnetoresistive Perovskites. *Nature (London)*, **386**, 256-259. <http://dx.doi.org/10.1038/386256a0>
- [2] Uehara, M., Mori, S., Chen, C.H. and Cheong, S.-W. (1999) Percolative Phase Separation Underlies Colossal Magnetoresistance in Mixed-Valent Manganites. *Nature (London)*, **399**, 560-563.
- [3] Kaul, S.N. (1985) Static Critical Phenomena in Ferromagnets with Quenched Disorder. *Journal of Magnetism and Magnetic Materials*, **53**, 5-53. [http://dx.doi.org/10.1016/0304-8853\(85\)90128-3](http://dx.doi.org/10.1016/0304-8853(85)90128-3)
- [4] Martin, M.C., Shirane, G., Endoh, Y., Hirota, K., Moritomo, Y. and Tokura, Y. (1996) Near-Edge X-Ray-Absorption Study of Transition-Metal-Implanted $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. *Physical Review B*, **53**, 9412. <http://dx.doi.org/10.1103/PhysRevB.53.9412>
- [5] Freitas, R.S., Haetinger, C., Pureur, P., Alonso, J.A. and Ghivelder, L. (2001) Static Critical Behavior of the Ferromagnetic Transition in $\text{LaMnO}_{3.14}$ Manganite. *Journal of Magnetism and Magnetic Materials*, **226-230**, 569-571. [http://dx.doi.org/10.1016/S0304-8853\(00\)00683-1](http://dx.doi.org/10.1016/S0304-8853(00)00683-1)
- [6] Shin, H.S., Lee, J.E., Nam, Y.S., Ju, H.L. and Park, C.W. (2001) First-Order-Like Magnetic Transition in Manganite Oxide $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. *Solid State Communications*, **118**, 377-380. [http://dx.doi.org/10.1016/S0038-1098\(01\)00123-5](http://dx.doi.org/10.1016/S0038-1098(01)00123-5)
- [7] Hong, C.S., Kim, W.S. and Hur, N.H. (2001) Transport and Magnetic Properties in the Ferromagnetic Regime of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$. *Physical Review B*, **63**, 092504. <http://dx.doi.org/10.1103/PhysRevB.63.092504>
- [8] Mira, J., Rivas, J., Rivadulla, F., Vazquez-Vazquez, C. and Lopez-Quintela, M.A. (1999) Change from First- to Second-Order Magnetic Phase Transition in $\text{La}_{2/3}(\text{Ca}, \text{Sr})_{1/3}\text{MnO}_3$ Perovskites. *Physical Review B*, **60**, 2998. <http://dx.doi.org/10.1103/PhysRevB.60.2998>
- [9] Anderson, P.W. and Hasegawa, H. (1955) Considerations on Double Exchange. *Physical Review*, **100**, 675. <http://dx.doi.org/10.1103/PhysRev.100.675>
- [10] Bau, L.V., Van Khiem, N., Phuc, N.X., Van Hong, L. and Nam, D.N.H. (2009) Magnetoresistance and Magnetocaloric Properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.95}\text{Mn}_{0.05}\text{O}_3$ Compound. *Journal of Physics: Conference Series*, **187**, Article ID: 012073.
- [11] Chau, N., Niem, P.Q., Nhat, H.N., Luong, N.H. and Tho, N.D. (2003) Influence of Cu Substitution for Mn on the Structure, Magnetic, Magnetocaloric and Magnetoresistance Properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Perovskites. *Physica B: Condensed Matter*, **327**, 214-217. [http://dx.doi.org/10.1016/S0921-4526\(02\)01731-3](http://dx.doi.org/10.1016/S0921-4526(02)01731-3)

- [12] Gam, D.T.H., Hai, N.H., Van Vu, L., Luong, N.H. and Chau, N. (2009) The Existence of Large Magnetocaloric Effect at Low Field Variation and the Anti-Corrosion Ability of Fe-Rich Alloy with Cr Substituted for Fe. *Journal of Physics: Conference Series*, **187**, Article ID: 012067.
- [13] Duc, N.H., Thanh, T.D., Tam, L.T.T., Tuan, B.M., Thanh, P.T., Yen, N.H., Long, P.T. and Dan, N.H. (2010) Study on Synthesis, Structure and Magnetocaloric Properties of $\text{CoMn}_{1-x}\text{Fe}_x\text{Si}$ Alloys. *Presented at the 5th International Workshop on Advanced Materials Science and Nanotechnology*, Ha Noi.
- [14] Zhang, Y.D., Zhang, P., Kim, K., Yu, S.-C., Dan, N.H. and Hou, X.L. (2010) Magnetic Properties and Giant Magnetocaloric Effects on the $\text{NiMn}_{0.9}\text{Sb}_{0.1}$ Compound. *Journal of the Korean Physical Society*, **57**, 1983-1986.
- [15] Bau, L.V., Khiem, N.V., Phuc, N.X., Hong, L.V., Nam, D.N.H. and Nordblad, P. (2010) Observation of Mixed-Phase Behavior in the Mn-Doped Cobaltite $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{1-x}\text{Mn}_x\text{O}_3$ ($x = 0-0.5$). *Journal of Magnetism and Magnetic Materials*, **322**, 753-755. <http://dx.doi.org/10.1016/j.jmmm.2009.10.054>
- [16] Kadano, L.P., Gotze, W., Hamblen, D., Hecht, R., Lewis, E.A.S., Palciauskas, V.V., Rayl, M., Swift, J., Aspnes, D. and Kane, J. (1967) Static Phenomena Near Critical Points: Theory and Experiment. *Reviews of Modern Physics*, **39**, 395. <http://dx.doi.org/10.1103/RevModPhys.39.395>
- [17] Fisher, M.E., Ma, S.-K. and Nickel, B.G. (1972) Critical Exponents for Long-Range Interactions. *Physical Review Letters*, **29**, 917. <http://dx.doi.org/10.1103/PhysRevLett.29.917>