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Slow thermodynamics in the phase separated state of the bilayered manganite $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$

Haruka Taniguchi[1]*, Yuma Nakamura[1], Takahisa Konno[1], Michiaki Matsukawa[1], and Ramanathaan Suryanarayanan[2]

[1] Department of Materials Science and Engineering, Iwate University, Morioka 020-8551, Japan
[2] Laboratoire de Physico-Chimie de L'état Solide, CNRS, UMR8182, Université Paris-Sud, 91405 Orsay, France

Abstract

Bilayered perovskite $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ exhibits a field-induced paramagnetic-insulator to ferromagnetic-metal transition, and a phase-separated state is realized after the field is switched off. In order to clarify the thermodynamic properties of the phase-separated state which is a common feature in many manganites, we performed specific heat measurement with field along the magnetization easy axis. We have revealed that the remanent specifc heat might exhibit a stretched exponential decay and the relaxation time is remarkably long. These results indicate the importance of magnetic frustration originating from the competition between double-exchange interaction and superexchange interaction.

Keywords: phase separation, manganite, thermodynamics, frustration

1 Introduction

Perovskite-type manganites fascinate many researchers with their various exotic phenomena. For example, bilayered $La_{2-2x}Sr_{1+2x}Mn_2O_7$ exhibits a charge/orbital ordered (CO/OO) state or a colossal magneto-resistance (CMR) effect [1]. In $La_{2-2x}Sr_{1+2x}Mn_2O_7$, Mn^{3+} and Mn^{4+} coexist and the ratio of Mn^{3+} to Mn^{4+} is $(2-2x)/2x$. Since one of the four $3d$ electrons of a Mn^{3+} occupies an e_g orbital in the perovskite structure, Jahn-Teller (JT) lattice-orbital effect acts on $Mn^{3+}O_6$ octahedra. In contrast, $Mn^{4+}O_6$ octahedra with empty e_g orbitals and half-occupied t_{2g} orbitals are free from JT effect. Therefore, at the half doping ($x = 0.5$), CE-type long-range CO/OO state in which the e_g electrons occupy the $3z^2 - r^2$ orbital is stabilized with the Neel temperature of 220 K [2, 3]. With decreasing x, the CO/OO correlation transforms into short-range one because of the mismatch between the number of Mn^{3+} and Mn^{4+}, and double-exchange (DE) interaction which induces itinerancy is enhanced [4, 5, 6, 7]. Thus, a charge frustration emerges and results in a metal-insulator transition and a CMR effect [8, 9, 10]. Lattice-orbital frustration also exists in this system: DE interaction makes the lattice structure homogeneous via itinerant electrons, whereas the coexistence of JT active $Mn^{3+}O_6$ and nonactive $Mn^{4+}O_6$ octahedra induces lattice inhomogeneity. Therefore, when the metallic phase is induced, $Mn^{3+}O_6$ octahedra shrink

*tanig@iwate-u.ac.jp

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along the c axis and e_g electrons transfer to the $x^2 - y^2$ orbital. Moreover, magnetic frustration plays an important role to determine the electronic state in $La_{2-2x}Sr_{1+2x}Mn_2O_7$: DE ferromagnetic interaction and superexchange (SE) antiferromagnetic interaction competes and a ferromagnetic-paramagnetic transition accompanies the metal-insulator transition [11].

We have been focusing on $La_{1.2}Sr_{1.8}Mn_2O_7$, which is close to the largest-CMR composition $x = 0.38$ [10] and the highest-Curie-temperature composition $x = 0.36$ [8], and on its Pr-substituted compound $(La_{1-z}Pr_z)_{1.2}Sr_{1.8}Mn_2O_7$. The substitution of Pr for La keeps the hole density constant and affects the lattice structure: it elongates MnO_6 octahedra along the c-axis [12]. As a result, the transition temperature of the paramagnetic-insulator (PMI) to ferromagnetic-metal (FMM) transition is suppressed and in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ the PMI phase is sustained down to 0 K [12, 13]. A FMM phase is induced in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ by magnetic field, accompanied by the lattice shrinkage along the c-axis similarly to the PMI-FMM transition in $La_{1.2}Sr_{1.8}Mn_2O_7$ [14]. Notably, the amplitude of the CMR effect in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ is as much as 6 orders of magnitude, which is highly enhanced compared with that in $La_{1.2}Sr_{1.8}Mn_2O_7$ (2 orders of magnitude) [15]. This result reflects the enhancement of the frustration which originates from the increase of short-range CO interaction by Pr-substitution. Interestingly, the temperature dependence of the magnetization is different between zero-field-cooling and field-cooling, suggesting spin-glass-like properties [16]. This result suggests the existence of a magnetic frustration in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. Another important feature is large hysteresis reported in the field dependence of thermal conductivity, magnetization, resistivity, and magnetostriction [16, 15, 13, 14, 17, 18]. These hystereses indicate the existence of the phase-separated phase after switching off a field.

In this study, to better understand the thermodynamic properties of phase-separated manganites, we measured the specific heat of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ under magnetic field and clarified the hysteretic behavior. Moreover, we investigated the time dependence of the remanent specific heat and estimated the relaxation time.

2 Methods

The single crystal of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ was grown from a sintered rod of the same nominal composition by the floating-zone method using an image furnace. The calculated lattice parameters of the tetragonal crystal structure of this crystal were shown in a previous report [16]. The mass of the sample cut out for the specific heat measurement is 73.0 mg. The dimensions of the sample are 3.4×3.0 mm^2 in the ab plane and 1.0 mm along the c axis. The direction of the c axis was determined by utilizing the fact that $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ cleaves along the ab plane.

Specific heat C was measured by a relaxation method using the Physical Properties Measurement System (PPMS, Quantum Design). The sample was mounted on the stage for the direction of magnetic field to be parallel to the c axis, which is the magnetization easy axis of the FMM phase [19]. The field-induced PMI-FMM transition of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ is of first-order, and electrons slowly transfer from the metastable FMM state to the stable PMI state when an applied field is reduced below the critical field H_c [16]. Thus, in order to obtain the virgin state in which only the PMI phase exists, before each measurement the sample was left above 200 K under zero field for about 2 hours and then cooled in zero field. Temperature-dependence measurements at fixed fields (0 and 6 T) were performed from 2.5 to 150 K. Field-dependence was measured in both increasing and decreasing field at the rate of 0.60 T/min, between 0 and 8 T for 2.5, 4, 6 and 8 K, and between 0 and 6 T for 10, 20 and 25 K. Moreover, since substantial remanent magnetic specific heat was observed, we investigated the relaxation of the remanent C at 20, 25 and 30 K, covering a large to small hysteresis region. The rate of the field sweep was 0.26 T/min, which was chosen as comparable as that for the relaxation measurement of remanent magnetization and magnetostriction in Ref. [14] and [17] in order to compare these

relaxation phenomena. The field sweep rate before the relaxation measurement of magnetization and magnetostriction was 0.26 T/min and 0.2 T/min, respectively.

3 Results

We successfully detected a field-induced transition in specific heat measurements. As shown in Fig. 1(a), the temperature dependence of C/T of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ differs between 0 and 6 T: C/T exhibits a peak at 88 K under 6 T, whereas there is no anomaly under 0 T. This anomaly is caused by the field-induced PMI-FMM transition.

Figure 1(c) and (d) represent the field dependence of the specific heat at several fixed temperatures. Here, the value of $C(H,T)$ is normalized by the specific heat before applying field, $C_{\mathrm{virgin}}(T)$. With increasing field, the specific heat is notably suppressed at a certain field, indicating the transition from PMI to FMM, which is accompanied by entropy reduction. The existence of large hysteresis between field-increasing and decreasing processes implies that the transition is of first-order. Interestingly, the specific heat does not recover completely even if the applied field is switched off. This result demonstrates that the PMI and FMM phases coexist with spatially separated. Focusing on the difference of $C(H)$ among different temperatures, $C(H)$ below 10 K exhibits a sharp step-like transition, whereas the transition above 20 K is broad and continuous. Similar step-like transition of specific heat is reported in cubic perovskite $La_{0.225}Pr_{0.40}Ca_{0.375}MnO_3$ [21]. However, to our knowledge, the relaxation of remanent specific heat had not been investigated yet in manganites.

Therefore, we focused on the remanent specific heat and clarified its relaxation at several temperatures as shown in Fig. 2(a). Δc_{R} is defined to represent the relaxation rate:

$$\Delta c_{\mathrm{R}}(t) \equiv (C_{\mathrm{R}}(t) - C_{\mathrm{R}}(0))/(C_{\mathrm{virgin}} - C_{\mathrm{R}}(0)) \quad . \tag{1}$$

Here, C_{virgin} and $C_{\mathrm{R}}(t)$ are the specific heat before field is applied and that when time passes by t after switching off the field, respectively. We have revealed that the relaxation curves are roughly fitted by stretched exponential functions:

$$f(t) = 1 - \exp(-(t/\tau)^{\beta}) \quad , \tag{2}$$

in which τ and β represent the characteristic relaxation time and exponent, respectively. The correlation coefficient r is 0.97 for 20 and 25 K, and 0.88 for 30 K. r indicates the accuracy of a fitting and ranges between 0 and 1: the larger r means the better fitness. Therefore, these fittings with $r \sim 1$ especially those for 20 and 25 K are considered to be successful. The relaxation described by a stretched exponential function, which is known to be applicable to spin glass, indicates that the relaxation process is complicated. Importantly, the relaxation time estimated from the fitting is remarkably long: τ exceeds one day with $\beta = 0.39$ at 25 K, for example.

4 Discussion

We consider that the origin of the step-like transitions in $C(H)$ below 10 K is the phase-separated ground state caused by frustration. When the FMM phase is realized partially, accompanying latent heat lowers H_{c} of the neighbor region. Here, H_{c} is defined as the field at which dC/dH exhibits a minimum. This reaction is repeated and results in an avalanche transition and a step-like drop of specific heat. We expect that the phase-separated ground state is mainly caused by the magnetic frustration between DE and SE interactions. Moreover, the lattice-orbital frustration between DE and JT interactions and the charge frustration between DE and CO interactions would also play an important role. These frustrations

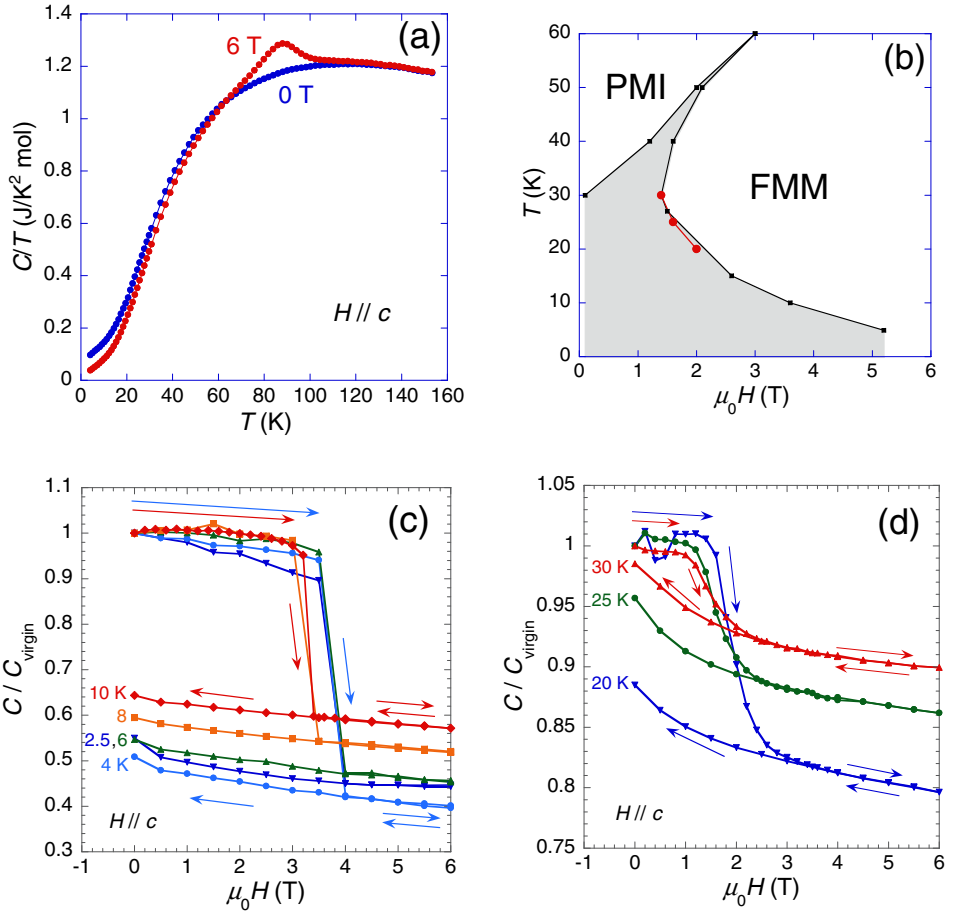

Figure 1: (a) Temperature dependence of C/T in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ under the field of 0 and 6 T along the c axis. C/T exhibits an anomaly only under 6 T, suggesting a field-induced PMI-FMM transition. (b) Field-temperature phase diagram of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. In the gray shaded area, in which c-axis magnetization and specific heat exhibit hysteretic behavior, a phase-separated state is realized. Red circles and black rectangles indicate transition points determined from the magnetic field dependence of specific heat (this study) and c-axis magnetization (Ref. [20] and [17]), respectively. Critical fields H_cs estimated from specific heat are defined as the field at which dC/dH exhibits a minimum in a field-scan measurement at a fixed temperature. (c, d) Magnetic-field dependence of the specific heat of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ at several temperatures. The field direction is parallel to the c axis and the field scan rate is 0.60 T/min. A substantial drop by applying field reflects the PMI-FMM transition.

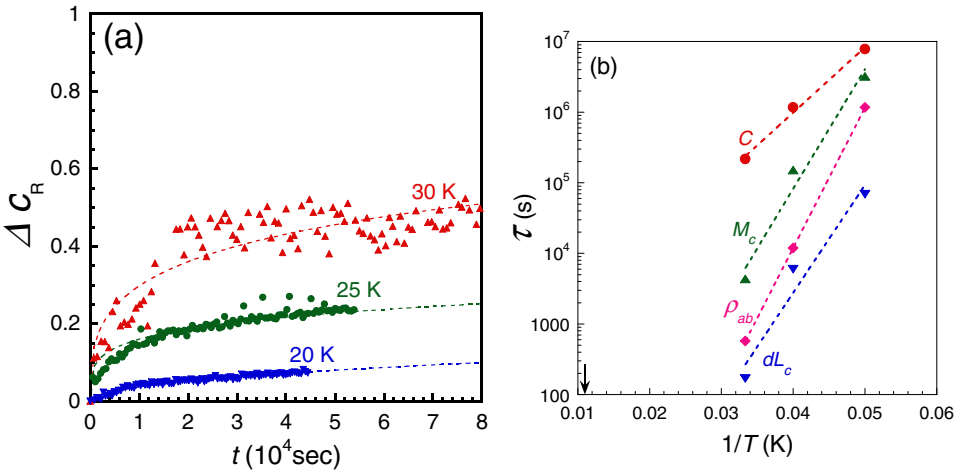

Figure 2: (a) The relaxation process of the remanent specific heat of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ after switching off the c-axis magnetic field of 6 T. Δc_R represents the relaxation rate, as the detail is mentioned in the main text. Each broken line demonstrates a stretched exponential function which is fitted into the experimental result at each temperature. (b) Comparison of the relaxation time of the remanent component in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ among the specific heat (this study), c-axis magnetization (Ref. [17]), ab-plane resistivity (Ref. [17]) and c-axis magnetostriction (Ref. [14]). Broken lines are fitted thermally-activated functions. For reference, the PMI-FMM transition temperature at 6 T defined as the peak temperature in $C(T)$ of Fig. 1(a) is indicated by the arrow.

enhance the instability of the PMI state under magnetic field and induces the transition to the FMM state at a field lower than the intrinsic value of critical field H_c.

For this reason, we expect that $C(H)$ in this study displays the intrinsic H_c above 20 K in which $C(H)$ exhibited a broad transition, and estimated H_c above 20 K as shown in Fig. 1(b). We have revealed in Fig. 1(b) that the thermodynamic phase diagram obtained from the specific heat coincides well with that from the c-axis magnetization [20, 17]. The transition shifts to a lower field with increasing temperature, similarly to the magnetization, magnetoresistance and magnetostriction in the same temperature range [16]. These results suggest that the field-induced transition has a thermally-activated character.

The tendency that the relaxation curve of remanent component might be fitted by a stretched exponential function is known to be true also for other physical quantities like magnetization [15, 14, 17], which is consistent with the existence of frustrations in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$ mentioned above. In

Fig. 2(b), the relaxation time τ estimated from the specific heat is compared with those from the *c*-axis magnetization [17], *ab*-plane resistivity [17], and *c*-axis magnetostriction [14].

We have clarified two common features among these τs: one is long τ, and the other is the temperature dependence described by a thermally-activated function, $\tau(T) = \tau_0 \exp(\Delta/k_B T)$. Long τ suggests strong frustration between competing interactions in $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. The thermally-activated-type temperature dependence of the relaxation time is consistent with the lower critical field at higher temperature in the same temperature range. The thermal activation energy Δ estimated from the fitting is of the same order among the four cases: 18 meV for specific heat, 34 meV for magnetization, 39 meV for resistivity, and 30 meV for magnetostriction.

The quantitative difference of τ among different physical quantities reflects the detailed difference among the phenomena detected in each measurement. A slow relaxation of remanent magnetization is caused by magnetic frustration between DE and SE interactions. The corresponding relaxation of remanent specific heat represents a slow decrease in the volume fraction of the FMM phase associated with a spontaneous transition from the FMM to PMI states. We believe that specific heat measurements reveal the entropy changes associated with phase transitions and provide direct information about the relaxation processes in phase-separated states of doped manganites. In contrast, additional factors are included in the relaxation of magnetization, resistivity, and magnetostriction. The factor for magnetization is the domain effect: even if the FMM phase sustains large volume, the relaxation rate increases when the alignment of the spin directions among domains is suppressed, resulting in the suppression of τ. In resistivity measurement, we should note that the relaxation rate is enhanced when a metallic path is destroyed. For magnetostriction, it should be noted that the lattice relaxation is not due to the structural transition associated with cooperative phenomena but arises from a local lattice distortion of MnO_6 octahedra without a long-range order. It is contrast to the relaxations in the thermodynamic, magnetic and transport properties which are taken as signatures of the phase transition from metastable FMM to stable PMI states in the long time scale. Additionally, at the higher temperature, a technical difficulty causes the larger discrepancy between τ estimated from specific heat and those from the others. Since specific heat C is measured using the relaxation method in this study, obtaining one value of C requires the longer time at the higher temperature: for example, about 13, 10 and 7.5 min was required at 30, 25 and 20 K, respectively. This time-passing effect will overestimate τ.

5 Summary

On the bilayered manganite $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$, which exhibits the field-induced paramagnetic-insulator to ferromagnetic-metal transition, we performed specific heat measurement of a single crystal under magnetic field along the *c* axis and examined the thermodynamic phase diagram and thermal relaxation process in the phase-separated state. In the field dependence, we have clarified a large hysteresis and a remanent component after switching off the field, which reflect the phase-separated character of $(La_{0.4}Pr_{0.6})_{1.2}Sr_{1.8}Mn_2O_7$. Moreover, we have revealed that the critical field below 30 K is enhanced with cooling. This result suggests the thermally activated character of this transition. In this study, what is new to the research field of manganites is the observation of the relaxation of remanent specific heat, which is expected to directly detect how the volume fraction of the metastable FMM phase is reduced. We have clarified that the relaxation curve is roughly described by a stretched exponential function and the relaxation time τ is remarkably long, which indicates the existence of a strong frustration. The main origin of this frustration is considered to be the competition between double-exchange and superexchange interactions.

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