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Electronic and magnetic instability in $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$

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Abstract

Electronic and magnetic instability in polycrystalline $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ manganite has been established from a systematic study of resistivity (ρ), magnetization (M) and specific heat (C). The sample shows a charge ordering transition at $T_{CO} \sim 200$ K, an antiferromagnetic (AFM) ordering transition at $T_N \sim 175$ K, a metal–insulator (MI) transition at $T_{MI} \sim 80$ K and an unusual magnetic ordering transition at $T_M^* \sim 45$ K in the absence of magnetic fields. Though the C data do not show any anomaly at T_{MI} for MI transition, these illustrate a much smaller anomaly than expected one at T_M* and is suppressed by magnetic fields. This indicates that the unusual magnetic ordering in this sample is of canted, fluctuated or phase separation of AFM and ferromagnetic in nature which is established from the $T-H$ phase diagram, as well as the thermal and magnetic hysteresis in ρ, M and C.

PACS: 75.30.V; 75.30.K; 75.60.E; 75.40.C

Keywords: Manganites; CMR; Phase instability

1. Introduction

The complicated phase diagram in colossal magnetoresistive (CMR) materials [1,2], $RE_{1-x}A_xMnO_3$ (RE = trivalent rare earths, A = divalent alkaline earth metals), arises due to the interplay between double exchange (DE) interaction and charge/orbital ordering (CO–OO). The interplay between DE interaction and CO–OO can be tuned by changing the value of x [1–3], by varying the radius of rare/alkaline earth metals [4], by applying electric/magnetic fields [5–7], by irradiating with X-ray/infrared radiation [8], by applying external pressure [9,10] and by Mn-site substitution [11–14].

Recently, it has been proposed that the ground state of CMR materials have electronic phase separation (PS), which is the simultaneous presence of sub-micrometer FM metallic phase percolated in an insulating charge ordering/

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antiferromagnetic (CO/AFM) matrix [15–20]. This PS scenario is of particular importance and favorable for the existence of out-of-equilibrium features. A little change of the fraction or the arrangement of the domains can induce the percolation. There is the possibility of emerging various interesting phenomena like time-dependent relaxation, two level fluctuation, non-equilibrium fluctuation, or relaxor ferroelectric behavior from the competition of the coexisting phases [15–20]. However, those phenomena were observed in different samples at various conditions. Though the Pr-based CMR systems have been widely studied [21–26], there is no report on the detection of instability in phases of these materials from the systematic study of transport, magnetic and thermal properties. Therefore, we chose an interesting system from our studied materials and thoroughly investigated the transport, magnetic and thermal properties to find out the electronic and magnetic instability in it.

In this article, we report the observation of electronic and magnetic instability in polycrystalline $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ manganite presumably due to spin fluctuations, canted FM spins or PS of AFM and FM domains. These are concluded to be the possible origins of the occurrence of an unusual magnetic ordering state below T_{MI} in it at low magnetic fields.

2. Experimental details

Polycrystalline $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ perovskite manganite was prepared by the standard solid-state reaction method from the powdered raw materials of Pr_6O_{11}, CaO, MnO_2 and $SrCO_3$. Homogenous combination of stoichiometric mixtures were heat treated at 900°C for 12 h, followed by regrinding and firing at 1200°C for 12 h. The resultant powders were palletized at a pressure $\sim 2\,\text{ton cm}^{-2}$ and sintered in air at 1350°C for 48 h with in-between grinding, palletizing and annealing for three times. Powder X-ray diffraction data obtained by SIEMENS D5000 diffractometer using CuKα radiation showed single phase of it. Electrical resistivity (ρ) was measured by the standard four-probe method. Magnetization (M) measurements were performed by the commercial SQUID magnetometer in temperature 10–300 K and magnetic field 0–8 T. A high-resolution AC calorimeter was utilized to measure the relative specific heat, C [27]. Absolute value of C was obtained by using a heat pulse thermal relaxation (HPTR) calorimeter [28] at low temperature (0.6–50 K). The hydrostatic pressure (P) dependent AC magnetic susceptibility (χ_{ac}) data were taken using the piston cylinder self-clamped technique [29]. It is noted that all data on ρ, M, and C were taken on cooling temperature unless when it is particularly specified for warming.

3. Results and discussion

Temperature variation of resistivity (ρ) of $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ at various magnetic fields (H) are shown in Fig. 1a. The MI transition becomes broader and the T_{MI} moves to higher temperatures with the increase of H, which is consistent with that observed in other systems [1,2]. The CO state is observed (as indicated by T_{CO} in Fig. 1a) up to a magnetic field of 2.5 T. Dependence of magnetization (M) on temperature at various applied magnetic fields (0.01–8 T) is shown in Fig. 1b. The ferromagnetic transition temperature (T_C), defined as the temperature where magnetization is saturated (indicated by arrow in Fig. 1b), rises with the increase of magnetic fields. Situation at 2 T is very different from others where magnetization starts to increase at $T \sim 200$ K, and exhibits a shoulder at $T \sim 175$ K, then increases and finally becomes saturated at $T \sim 80$ K though these transitions are not so vivid from temperature variation of ρ at 2 T (Fig. 1a).

The temperature dependence of specific heat (C) generally accounts for the anomalies corresponding to different thermodynamic phase transitions [23]. It is a bulk property and shows a rather small (or undetectable) anomaly due to minor impurity, short range or meta-stable ordering phases. Fig. 2 illustrates the temperature distinction of C for this sample at diverse magnetic fields (0–8 T), where anomalies owing to AFM, CO and FM transitions are noticed, respectively, at T_N, T_{CO} and T_C. The AFM and CO anomalies are clearly observed up

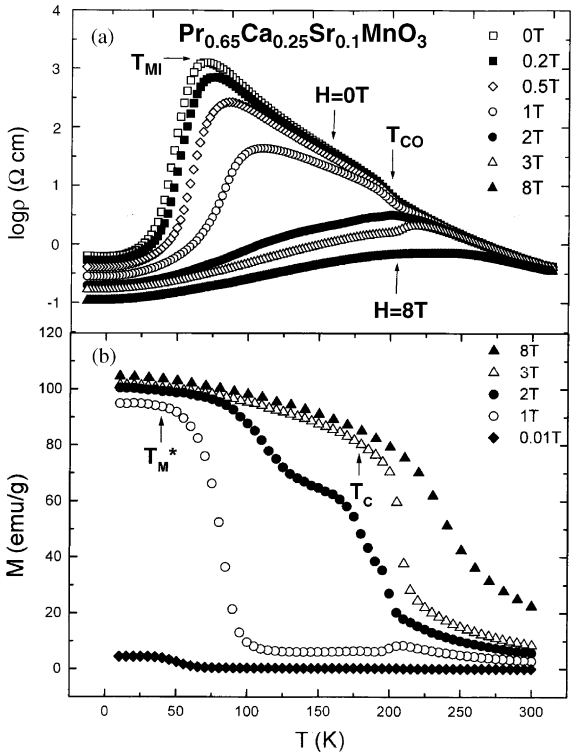

Fig. 1. Temperature dependence of (a) resistivity (ρ) in logarithmic scale and (b) magnetization (M) for $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ sample at various magnetic fields (0–8 T). The charge ordering (T_{CO}), metal–insulator (T_{MI}), ferromagnetic (T_C) and unusual magnetic ordering (T_M^*) transition temperatures are indicated by arrows. For clearness, some data curves are removed.

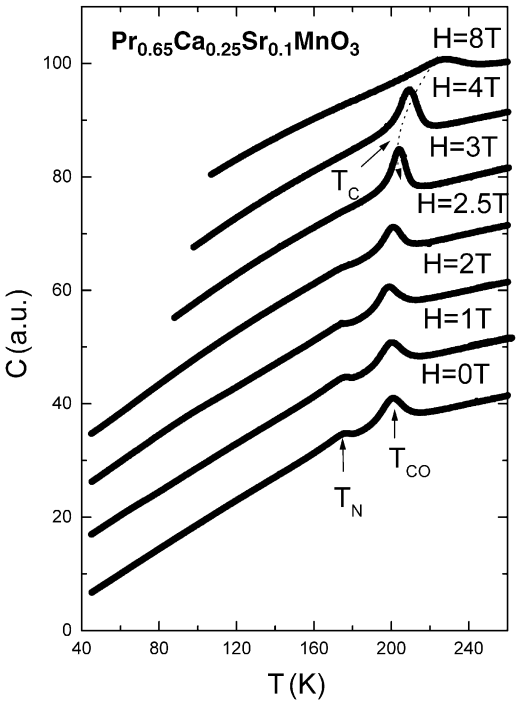

Fig. 2. Temperature variation of specific heat (C) for $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ sample at various magnetic fields (0–8 T). The anomalies corresponding to charge ordering (T_{CO}), antiferromagnetic (T_N) and ferromagnetic (T_C) transitions are pointed out by arrows.

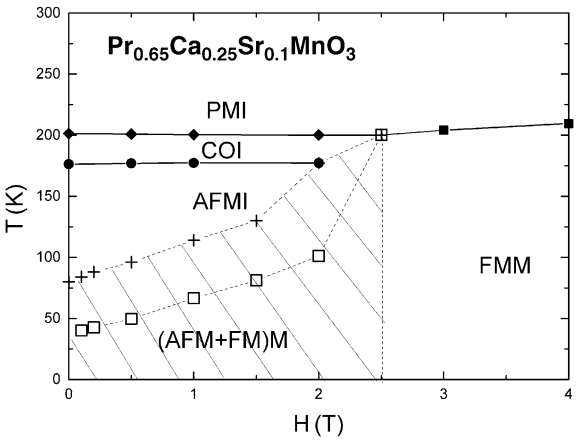

Fig. 3. Phase diagram ($T-H$) for $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ drawn on the basis of the results of Figs. 1 and 2. (AFM + FM)M states are represented by the shaded region.

to 2.5 T and the FM anomalies are detected from 3 to 8 T (Fig. 2). These observations are in accordance with the data demonstrated in Figs. 1a and b. However, from Fig. 2 we could not successfully resolve any specific heat anomaly at $T_{MI} \sim 80$ K (for details, see Fig. 6). We thus speculate that the magnetic ordering state at low magnetic fields and low temperatures (below T_{MI}) in this sample is very unusual and denoted as mixing (AFM + FM)M. According to the results of Figs. 1 and 2, the $T-H$ phase diagram of this manganite is shown in Fig. 3, where paramagnetic insulating (PMI), charge-ordered insulating (COI), antiferromagnetic insulating (AFMI), ferromagnetic metallic (FMM) and unusual magnetic metallic (AFM + FM)M regions are clearly indicated. The unusual mixed (AFM + FM)M state may be due to electronic and magnetic instability or the PS of AFM and FM domains in the sample below T_{MI}

at low magnetic fields. In the following paragraphs, we present more detailed data and further discuss these phenomena.

3.1. Detection of the unusual magnetic state in $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$

It is fascinating to note that the maximum magneto-resistance MR $= -[\rho(H) - \rho(0)]/\rho(0)$ at 70 K (near its T_{MI}) obtained from Fig. 1a is as high as 50%, 80% and 99% correspondingly at low magnetic fields of 0.1, 0.2 and 0.5 T. This may be due to a particular unstable mixing phase of a weak CO insulating at high temperatures and a (AFM + FM)M phase at low temperatures in it. Therefore, the application of a low magnetic field ($\leqslant 0.5$ T) is enough to partially melt the CO phase and percolate the FM state to enhance the metallicity. Hence, the large enhancement of MR indicates its electronic and magnetic instability or PS below its T_{MI} at low magnetic fields. This is an indirect evidence that the lattice distortion accompanied with AFM/CO plays an important role to exhibit a huge MR in CMR systems.

Fig. 4 shows the hydrostatic pressure (P) dependent AC magnetic susceptibility (χ_{ac}) measured in warming temperature from 80 to 280 K. At ambient pressure, there is a very small anomaly at 200 K owing to CO transition. With the increase of P, the temperature dependent χ_{ac} profile

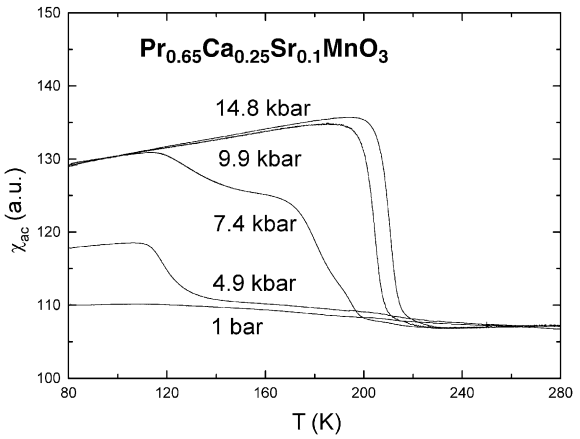

Fig. 4. Hydrostatic pressure (P) dependent AC magnetic susceptibility (χ_{ac}) measured at warming temperature from 80 to 280 K.

becomes very similar to that of temperature dependent magnetization in various magnetic fields (Fig. 1b). The behavior for pressure of 7.4 kbar on AC susceptibility is almost the same as that of magnetic field of 2 T on magnetization shown in Fig. 1b. A sharp transition due to FM ordering is observed at $T_C \sim 200$ K for the pressure of 9.9 kbar. This is similar to that observed in $Pr_{0.7}Ca_{0.3}MnO_3$ [26] and $(Nd_{0.6}La_{0.4})_{0.5}Sr_{0.5}MnO_3$ [30]. However, this is in contrast with that observed in $(Nd_{1-y}Sm_y)_{0.5}Sr_{0.5}MnO_3$ (for $y = 0.875$) where the pressure induces the CO transition and increases T_C [9]. Basically, the external pressure can stabilize the structure (reduce the distortion) and suppress the spin fluctuations in perovskite manganites [31]. It can also melt the CO state and transform the system from PMI to FMM state [26]. Therefore, it is reasonable to see the increase of T_C due to the increased connectivity among the meta-stable FM domains by melting of CO states with the increase of pressure. This also designates the electronic and magnetic instability in this sample due to spin fluctuations or PS below T_{MI}.

The magnetic hysteresis of ρ and M at a fixed temperature of 10 K are shown in Fig. 5. Here, the sample was first cooled down to 10 K at zero magnetic field, then the resistivity and magnetization measurements were taken by sweeping the applied magnetic field up and then down. The resistivity decreases with increasing magnetic fields. It slightly increases from the minimum value in the course of decreasing magnetic fields and the irreversibility occurs at $H \sim 3$ T. Magnetization curves also show similar irreversible performance at a lower magnetic field of ~ 2 T. In the absence of magnetic field, the FM spins may be canted, or meta-stable, or fluctuating, or mixed with AFM spins, in this sample. So the magnetization is small as the H is small during increasing and decreasing of magnetic fields. But the FM spins are better aligned, the spin fluctuations are decreased and perhaps the long-range FM order is achieved above 2 T confirming the saturation of magnetization and resistivity. Hence it is once more specified that the canted or fluctuated FM spins are stabilized above 2 T and long range FM ordering is achieved. It is noted that both the ρ

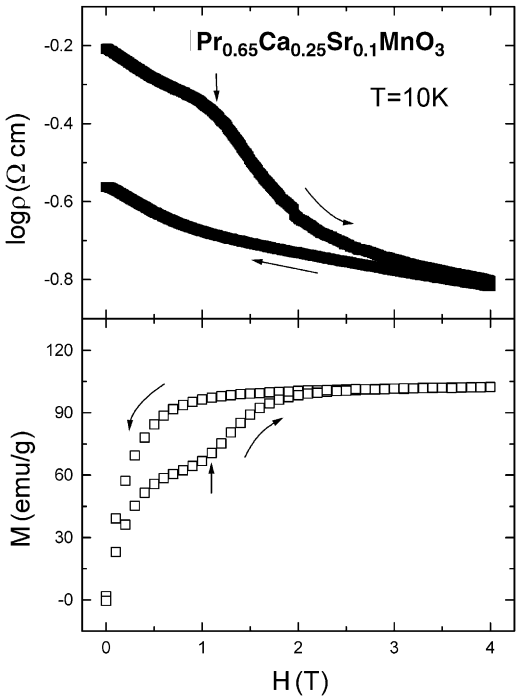

Fig. 5. Magnetic hysteresis of resistivity (ρ) in logarithmic scale and magnetization (M) at a fixed temperature (10 K). The curves during sweeping up and down the magnetic fields are indicated by arrows. The kinks in ρ and M around 1 T are denoted by arrows.

and M curves exhibit a kink at a magnetic field of approximately 1 T (indicated by arrows in Fig. 5) in the sweeping up mode. Similar kink in magnetization at 13 K is also detected by Tomioka et al. [32] at a higher magnetic field (3–4 T) in a $Pr_{0.7}Ca_{0.3}MnO_3$ single crystal, which is insulating at all temperatures in the absence of magnetic field. The authors [32] have explained this as the irreversible turn out of canted AFM to FM states and are confirmed from the temperature variation of resistivity curves. The magnetic field dependent resistivity of $Pr_{0.7}Ca_{0.3}MnO_3$ single crystal at 13 K [32] is different from that of our sample at 10 K. In Ref. [32], there is a sharp drop of resistivity (10 orders of magnitude) around 3–4 T (where the kink in magnetization is observed) during the field sweeping up and the resistivity is not increased from the minimum value with the field sweeping down, confirming the irreversible turn out of canted AFM spins to FM ones. However, in our sample the kink of resistivity is observed at 1 T (where the kink in magnetization is also observed) and the ρ slightly increases with the field sweeping down. Therefore, it is likely that the kink in our system is the transformation of canted or fluctuated FM to FM. This implies that the transport mechanism in $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ is somewhat different from that in $Pr_{0.7}Ca_{0.3}MnO_3$ single crystal [32] and possibly due to the electronic and magnetic instability or the probable PS of AFM and FM state.

The final verification on the electronic and magnetic instability in $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ below T_{MI} at low magnetic fields is attained from the C/T vs. T curves (Fig. 6). It is well established [1,2] that the CO insulating state is unstable under high magnetic fields and a MI transition leading to FMM state can take place due to the melting of CO insulating state. Generally, the FM transition temperature (T_C) and the MI transition temperature (T_{MI}) are close to each other [1,2]. Compre-

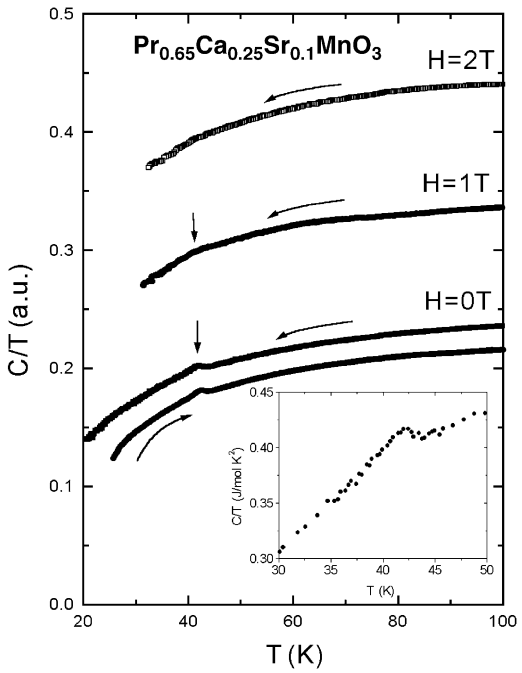

Fig. 6. C/T vs. T curves at different magnetic fields (0–2 T). The unusual magnetic transition temperature (T_M^*) and the data during cooling and warming are indicated by arrows. The inset shows the absolute C/T vs. T measured by HPTR calorimeter at zero field.

hensible anomalies should be observed in C because of stable FM phase transitions [23]. Within this scenario, the absence of anomaly in C near T_{MI}, the presence of small specific heat anomaly at T_M^* and the substantial difference between T_{MI} and T_M^* would indicate the instability of the (AFM + FM) state below T_{MI}. Here the FM metallic phases may be percolated to the CO/AFM matrix. Fig. 6 shows no anomaly at $T_{MI} \sim 80$ K corresponding to MI transition (observed in Fig. 1), but demonstrates a rather smaller than expected one at $T_M^* \sim 45$ K (shown by arrow in Fig. 6) at low magnetic fields ($\leqslant 1$ T). The zero field C data taken in cooling and warming illustrate that the anomalies occur at same temperature (T_M^*) without resolvable hysteresis. The inset of Fig. 6 shows the absolute values (taken by HPTR calorimeter) of discrete C/T data of the sample at zero magnetic field, in which the anomaly around 45 K is further confirmed. The approximate magnitude of jump seen in the specific heat (ΔC) estimated from the inset of Fig. 6 at $T_M^* \sim 45$ K is only about 0.85 J/mol K, whereas that of CO transition at zero field (Fig. 2) is about 19 J/mol K. The ΔC associated with the magnetic ordering transition at $T_M^* \sim 45$ K (Fig. 6) is also much smaller than that of a typical FM transition (30.4 J/mol K) at $T_C \sim 200$ K and $H = 3$ T (Fig. 2). In addition, this small anomaly (0.85 J/mol K) due to unusual magnetic transition is also smeared at $H = 1-2$ T (Figs. 2 and 6) but resumes at $T_C \sim 200$ K and $H = 3$ T (Fig. 2). Thus we speculate that the unusual magnetic ordering state in $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ below $T_{MI} \sim 80$ K at low magnetic fields is different from that of a typical FMM state. Moreover, the existence of unusual magnetic ordering state in this sample below $T_{MI} \sim 80$ K reflects the electronic and magnetic instability in nature due to canted, fluctuated or the PS of AFM and FM.

4. Conclusions

From the systematic studies on the temperature and magnetic field dependence of resistivity, magnetization, pressure effect and specific heat of polycrystalline $Pr_{0.65}Ca_{0.25}Sr_{0.1}MnO_3$ perovskite manganite, it has been confirmed that the sample shows an unusual magnetic metallic state below T_{MI} at low magnetic fields. This unusual state is clearly identified in $T-H$ phase diagram (shaded area in Fig. 3) using various measurements. It has been explained that the unusual magnetic ordering state in this sample is due to the electronic and magnetic instability resulted from the interplay between the CO/AFM insulating state and FM metallic state. Our results have also clearly demonstrated that the spins in this region may be canted, fluctuated or possible PS of AFM and FM in nature and can be stabilized by applying magnetic field or external pressure to achieve the long range FM state.

Acknowledgements

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