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Magnetotransport properties of $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ $(y=0.0-0.7)$ showing crossover from A-type to CE-type antiferromagnetic state

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Resistivity and thermoelectric power (TEP) of $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ $[y=0.0-0.7]$, both in the presence and in the absence of magnetic field, have been reported. With the increase of Pr content metal-insulator transition (MIT) temperature T_p decreases while magnetoresistance increases. A little above T_p, thermoelectric power shows a peak at a temperature $T_{\max}$ (say) indicating existence of the A-type AFM phase for the samples with smaller $y<0.7$. Again with higher Pr content $(y>0.2)$, an additional peak is observed at $T^*_{\max}$ $(T^*_{\max}<T_p<T_{\max})$. This additional peak is a resultant effect of the increase of orbital degrees of freedom (arising from collective Jahn-Teller distortion at higher Pr-concentration) and the decrease of entropy of the charge carriers (arising due to the spin polarization in the FM phase). The present system shows a changeover from the A-type AFM state to the CE-type AFM state at a ‘‘critical’’ concentration between $y=0.6$ and 0.7. The magnetothermopower data establish well the orbital ordering in the $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ type CMR system.

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I. INTRODUCTION

The ABO_3 type doped manganite perovskites viz., $R_{1-x}D_xMnO_3$ (with R: rare earth metal and D: alkaline earth metal) have been extensively investigated in recent years because of their colossal magneresistive (CMR) properties.[1] Simultaneous appearance of ferromagnetic (FM) and metallic behavior in these systems is attributed to the double exchange (DE) interaction between the pairs of Mn^{3+} and Mn^{4+} ions.[2] Substitution of cations with different sizes at the rare earth sites results in a lattice distortion that influences the FM double exchange and the antiferromagnetic (AFM) superexchange interactions. Recently, it has been demonstrated that microscopic phase separation plays an essential role in the physics of the rare earth manganites.[3–5] Essentially, it results in the apparent percolative character of the insulator-metal transition when the transition is from the charge-ordered insulating to the FM metallic state. Here one observes the largest change in resistivity (more than 4 orders of magnitude) and, therefore, the largest magnetoresistance. Even a small distortion of the atomic arrangement and hence the domain structure can induce percolation.

The $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$ type system, where La is partially substituted by Pr having a smaller ionic radius, turns out to be one of the most convenient systems for studying the phase separation behavior. The Pr riched composition corresponds to a very stable charge ordered AFM phase, whereas the compositions with high La content are FM metals. For the $Pr_{1-x}Ca_xMnO_3$ compositions, close to $x=0.3$, existence of phase separation is well proven from the study of MR, magnetization and specific heat.[6,7] The magnetic phase diagram in $Pr_{1-x}Ca_xMnO_3$ presents different states depending on the concentration (x). For higher Mn^{3+} content, the compound is FM at lower temperature $(x\sim0.2)$ and for larger x-values $(x>0.4)$ they are CE-type orbitally ordered AFM.[8] In between these compositions, a mixing of FM and AFM phases is observed by Neutron diffraction.[9] Moreover, at a fixed Ca-concentration of $x=0.3$ in $(La_{1-y}Pr_y)_{1-x}Ca_xMnO_3$, the variation of La/Pr ratio (y) leads to the transition between FM metal and charge ordered insulating state[10] at $y\sim0.7$. Near this phase boundary, a rather wide region of phase separation was observed directly by electron diffraction and electron microscopy.[11] A thorough investigation of this $Pr_{0.65}(Ca_ySr_{1-y})_{0.35}MnO_3$ composition by neutron diffraction has been done by Blake *et al.*[12]

In spite of the large amount of work devoted to the manganites, the microscopic nature of the phase-separated state has not been well understood. For example, the electronic property of the constituent phases as well as their volume fraction and spatial distributions in the sample remain to be characterized. More importantly the physical mechanism underlying the phase separation phenomenon still remains unclear. To address these basic queries, the microscopic structure of manganites must be characterized in detail. In this regard field dependent resistivity and Seebeck coefficient play an important role.

In this paper we report the thermal behavior of thermoelectric power (TEP) and resistivity of $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ $[y=0.0-0.7]$ both in the presence and absence of magnetic field. Variation (decrease) of tolerance factor (t) has also been studied. The samples with $y=0$ and 1 are, respectively, FM metal and charge ordered AFM insulator. Concentration dependent changeover from metallic to insulating state has been studied throwing more

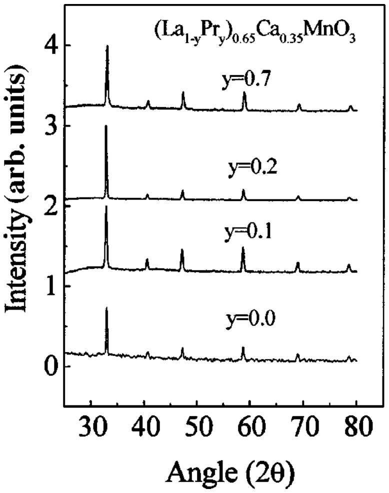

FIG. 1. X-ray diffraction pattern for $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ with $y=0.0$, 0.2, 0.3, and 0.7. All are showing single phases.

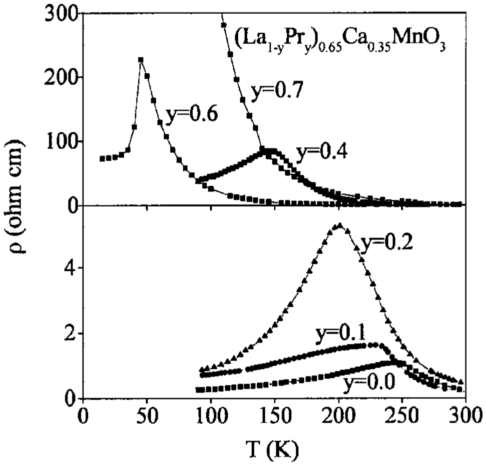

FIG. 2. Temperature dependent resistivity for $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ [with $y=0.0,0.1,0.2,0.4,0.6,0.7$].

light on phase separation behavior. Special attention has also been paid on the study of TEP, which is found to be one of the most sensitive parameters to address the nature of the carriers in the system.

II. EXPERIMENT

Different compositions of the ceramic samples $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ [$y=0.0$–0.7] were prepared by conventional solid state reaction method. Stoichiometric amounts of high purity La_2O_3, Pr_6O_{11}, $CaCO_3$, $\{Mn(CH_3COO)_2,4H_2O\}$ were thoroughly mixed, ground and then preheated twice, once at 500 °C for 5 h and then at 900 °C for 24 h. The fine ground powder was then annealed at 1200 °C again for 24 h and furnace cooled at a steady rate of 5 °C/min. The final ground powder was palletized and further heated at 1250 °C for 24 h and then cooled at the same rate. The single-phase character of all the samples was confirmed by XRD study with Cu $K\alpha$ radiation.

Resistivity of the samples was measured by conventional four-probe method. The bulk samples were cut into definite rectangular shape and the electrical connections were made by good quality silver paint. Data have been taken for both forward and reversed current directions to minimize offset voltage and thermal effect. Thermoelectric power was measured by standard differential technique[13] in the temperature range 80–300 K. Temperature was measured with an accuracy of 0.5 K.

III. RESULTS AND DISCUSSION

The XRD pattern shown in Fig. 1 indicates single-phase character of all the samples. The resistivity vs temperature curves for the $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ samples of different compositions are shown in Fig. 2. It is seen that in the concentration range $0 \leqslant y \leqslant 0.6$ (where tolerance factor $t=0.91631$ for $y=0.0$ and 0.91127 for $y=0.6$), there is an insulator to metal transition while for the samples with $y \geqslant 0.7$ no such transition is observed. It is also noticed that with the increase of Pr content (i.e., with decrease of t) resistivity increases and metal to insulator ($M-I$) transition temperature (T_p) decreases and finally T_p disappears at $y=0.7(t=0.91043)$ in the temperature range (20–300 K). The T_p also decreases systematically and almost linearly from 240 to 50 K for all the samples with concentration varying from $y=0.0$ to 0.6.

For detailed analysis of the resistivity (ρ) data, the $\rho(T)$ curve below T_p are fitted with different theoretical models[14] and we notice that the equation $\rho(T)=\rho_{0+}\rho_{2.5}T^{2.5}$ (where $T^{2.5}$ term implies the carrier magnon scattering) fits well with the experimental data. It is seen from Fig. 3 that the low temperature ($T<T_p$) resistivity data for the samples with $x \leqslant 0.6$ showing metal–insulator transition, fit very well with the above equation indicating that the metallic region is actually in the FM phase. It is also observed that the best-fit

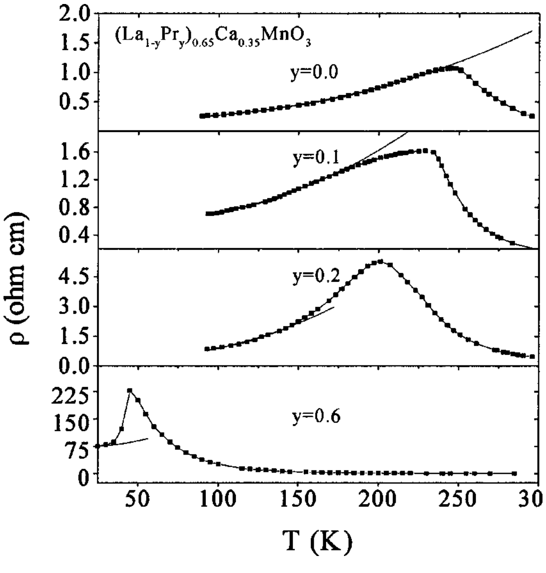

FIG. 3. $\rho(T)=\rho_0+\rho_{2.5}T^{2.5}$ has been fitted in the resistivity curve below T_p for the system $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$. The solid line corresponds to the best-fit region. The best-fit region decreases with the increase of Pr content. Fitted curves have been shown for $y=0.0$, 0.1, 0.2, and 0.6.

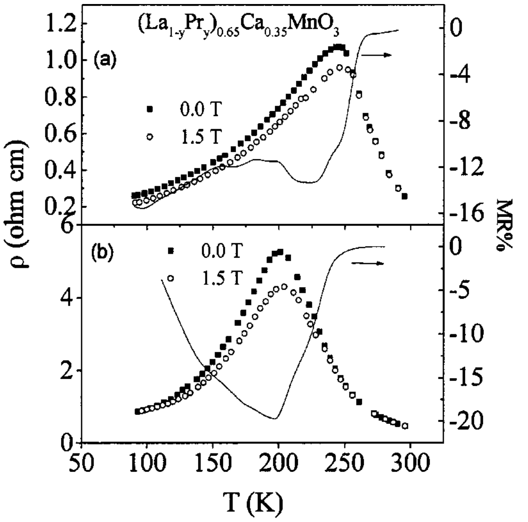

FIG. 4. Thermal variation of resistivity of $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ (a) for $y=0.0$ at zero magnetic field, $B=0$ (solid circle) and at a magnetic field $B=1.5$ T (open circle) and (b) for $y=0.2$ at zero magnetic field, $B=0$ (solid circle) and at a magnetic field $B=1.5$ T (open circle). Solid curves are for thermal variation of magnetoresistance.

region of the $\rho(T)$ curve decreases with increasing Pr content suggesting decrease of the FM phase with the increase of Pr content. The above analysis is a signature of phase separation, that is, coexistence of ferromagnetic metallic (FMM) and charge ordered (CO) insulating states in the Pr doped system.

The effect of magnetic field on resistivity and hence the corresponding magnetoresistance (MR) of the samples of different compositions are shown in Fig. 4. The MR is estimated from the relation $[\rho(H)-\rho(0)]/\rho(0)$ [where $\rho(0)$ is the resistivity at zero field and $\rho(H)$ is the resistivity at magnetic field H]. Application of magnetic field causes decrease of resistivity around the transition temperature and a shift of T_p towards the higher temperature region is observed. The negative MR% (at 1.5 T field) increases with increasing Pr content. In addition, the estimated dT_p/dH of the parent compound $(y=0)$ is about $\sim 3K/T$ and increases with increase of y which is consistent with the previous reported values.[15,16] The MR data presented in Fig. 4 show a maximum at a temperature T_{mr} (say) which is little lower than the corresponding metal insulator transition temperature T_p. It is obvious from the above data that MR enhances largely as the metallicity decreases. So it can be concluded that the large MR region can be clearly understood when the various effects which are in competition with double exchange are considered. Therefore, to achieve a large MR effect, the insulating phase is at least as important as the metallic one and the most interesting region is the metal to insulator boundary.[17,18] The above discussion is consistent with the relevant phase separation mechanism.

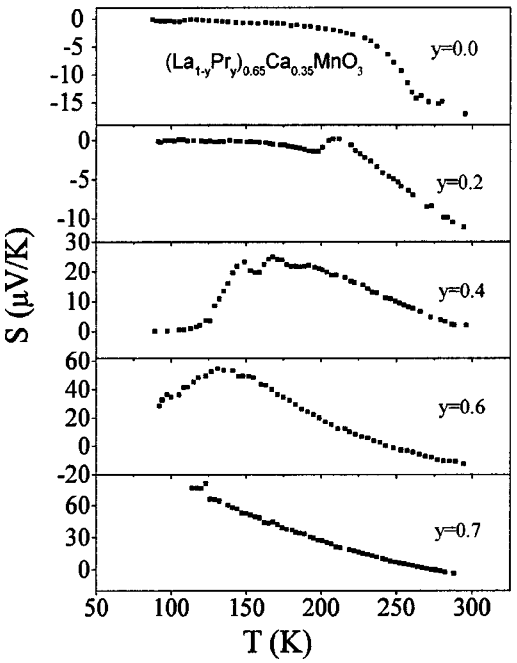

FIG. 5. Thermal variation of thermoelectric power for $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ [with $y=0.0$,0.2, 0.4, 0.6, and 0.7].

A stronger support of the phase separation comes from the temperature dependence of thermoelectric power (TEP) of $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ (with $y=0$, 0.2, 0.4, 0.6, and 0.7) of these samples is shown in Fig. 5. We notice an appreciable change of TEP (S) behavior with Pr content. For the undoped sample with $y=0$, it is found that as the temperature decreases, TEP value decreases abruptly and becomes more or less saturated to ~ 0 μV/K below a certain temperature ($T \sim 240$ K). For the sample with $y=0.2$, a crossover from negative to positive S value takes place around 225 K. Here seebeck coefficient $S(T)$ shows a maximum around $T_{\max}$ ($\sim$220 K) and then with decreasing temperature it shows a minimum at $T_{\min}\sim$200 K. With further decrease of temperature $S(T)$ first increases and then becomes saturated similar to the behavior shown by the undoped composition (with $y=0$). The value of $S(T)$ for $y=0.4$ shows interesting double peaks. The first peak appears at around $\sim$160 K ($T_{\max}$) with a minimum at $\sim$150 K ($T_{\min}$) and then the second peak appears at $\sim$145 K ($T^*_{\max}$). Finally, with further decreasing temperature, $S(T)$ first decreases and then becomes saturated to almost ~ 0 μV/K at 125 K. For the sample with $y=0.6$, the $S(T)$ value changes sign from $-ve$ to $+ve$ at $\sim$240 K and it gives a maximum value at $\sim$130 K. As temperature decreases further, S value also decreases down to 90 K, the minimum temperature range of our measurement. The $S(T)$ value of the sample with $y=0.7$, showing no metal–insulator transition, changes sign at around 260 K and then it increases monotonically with decreasing temperature. The Seebeck coefficient of the Pr free $y=0$ sample is consistent with that reported by Hundless *et al.*[19] It is seen that as Pr content increases, TEP value increases. In the case of strong coupling between holes and magnetic spins, the TEP is given by 1/3($\eta\Delta C_m/eN$) (where N is the hole-concentration and η is a measure of the coupling of spin entropy of carriers, ΔC_m is the magnetic specific heat[20]). Qualitatively, a decrease of TEP indicates an increase in N. Therefore, in the system of our present investigation, TEP value increases with the increase of Pr content causing a decrease of mobile carrier concentration. This is a signature of localization of the carriers (increase of resistivity). It is interesting to mention that the low temperature ($T<T_p$) thermopower is $+ve$ for all the samples. Near the resistive transition (for $y=0.0-0.6$) temperature T_p, TEP collapses sharply to a lower value (almost zero value), a characteristic of metallic conduction.

Though the low temperature TEP data of all the samples behave in a similar fashion, one finds an interesting and pronounced difference between TEP data near and above T_p. If the transport is dominated by carriers in the vicinity of the Fermi energy and we neglect the spin dependent contribution (since at low temperature in the metallic region spins are orderly oriented), the Seebeck coefficient can be expressed in terms of the energy derivative of the conductivity viz.,

$$S=(\pi^2k^2T/3e)[\partial \ln \sigma(E)/\partial E]_{E=E_F},$$

where k is the Boltzmann's constant, e is the charge of an electron, σ is the conductivity, which is determined by the integral over isoenergetic surfaces of the product of the scattering time and the Fermi velocity. In the low temperature spin ordered state, a local spin density approximation calculation yields a nearly half metallic band structure with a high density of states in the partially filled Mn-derived lower energy majority spin bands.[21] The relatively large bandwidth dominant spin majority bands suggests weak energy dependence to the conductivity, consistent with the small magnitude of TEP at low temperature. Therefore, as Pr content increases the bandwidth decreases and the value of S at low temperature increases.

The temperature dependence of S for the sample with $y=0.2$ differs significantly from that of the Pr free sample (with $y=0$). For the undoped sample, the T_p corresponds to the point of maximum dS/dT. On the other hand, for sample with $y=0.2$, a decrease in diffusive thermopower contribution marked by an approximately $\sim T$ behavior is observed only within small temperature range between $T_{\max}$ and $T_{\min}$. Comparing the experimental data of $\rho(T)$ and $S(T)$ we find $T_{\min}$ coincides with T_p. The observed peak at $T_{\max}$ is a signature of A-type AFM phase. Similar thermopower behavior has also been observed by Nakamae *et al.*,[22] in bilayered manganite and they have suggested that the peak is due to the presence of A-type AFM phase. It was reported earlier by Chatterjee and Nigam[23] that with decreasing A-site ionic radius in the manganites, the system gradually changes from FM state to A-type AFM state and then to CE-type AFM state and finally to spin glasslike state. Therefore, in the present investigation one might expect that with doping Pr, A-type AFM would appear. The $S(T)$ value of the sample with higher Pr content viz., $y=0.4$ also shows at $T_{\max}$ and $T_{\min}$ similarly to those shown by the $y=0.2$ sample. Interestingly, in addition to the single peak shown by the $y=0.2$ sample around $T_{\max}$, the $y=0.4$ sample shows an additional peak around $T^*_{\max}$ (say). $T^*_{\max}$ is lower than $T_{\max}$. Like the $y=0.2$ sample, the $T_{\max}$ of the sample with $y=0.4$ again suggesting the presence of A-type AFM ordering. The presence of $T^*_{\max}$ can be explained as follows. As Pr content increases ($y\geqslant 0.4$), the collective J-T distortion increases below T_p, weakening the orbital stability. As a consequence, the interaction between charge carriers and orbital degrees of freedom increases. On the other hand, the spin degrees of freedom is lost due to the spin polarization in the FM state, thus cannot contribute to an increase in the entropy of the charge carriers. The balance between these two opposing effects may produce the second peak at $T^*_{\max}$. It is important to mention here that as Pr content increases orbital ordering also increases and because of that a second peak in $S(T)$ becomes more prominent.

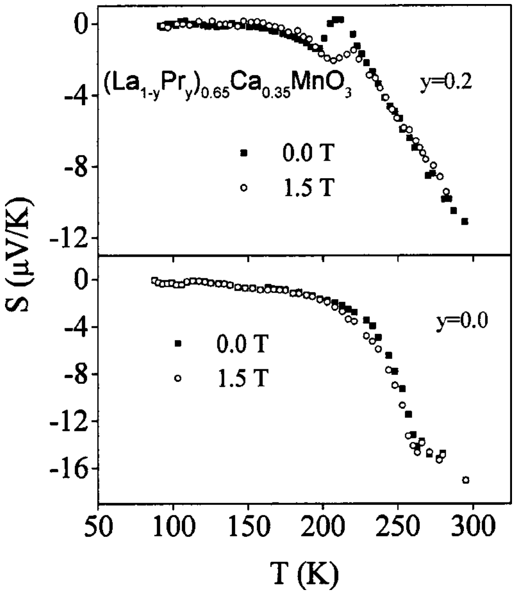

FIG. 6. Thermal variation of thermoelectric power at zero magnetic field ($B=0$) and at a magnetic field $B=1.5$ T for $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ with $y=0$ and 0.2.

Because of the constraint of low temperature (<90 K) TEP measurement in our present set-up, we cannot show the low temperature behavior of $S(T)$ for the sample with $y=0.6$ for which $T_p\sim 50$ K. The observed peak around ~ 140 K for this sample is also considered to be due to the existence of A-type AFM state as in the samples with $y=0.2$ and 0.4. It is worth mentioning that the $S(T)$ value of the semiconducting sample ($y=0.7$) does not show any maximum within the temperature range of $S(T)$ measurement. The absence of maximum for the sample with $y=0.7$ without showing any metal–insulator transition, indicates that this system is a CE-type antiferromagnet. Thus a concentration (y) dependent changeover from the A-type AFM state to a CE type antiferromagnetic (charge ordering state) state occurs around a critical concentration $y>0.6$. The large increase ($\geqslant 10^4$) of resistivity above this critical concentration also supports the occurrence of the CO-state. Thus from the above discussion of the magnetic field independent TEP data it is obvious that with increasing Pr content, the FMM phase decreases and antiferromagnetic insulating (AFMI) region increases clearly indicating the existence of phase separation.

The magnetic field dependence of TEP data for $y=0$ and $y=0.2$ is shown in Fig. 6. For the Pr free ($y=0$) sample application of the magnetic field causes a decrease of $S(T)$ value. But below a certain temperature, the $S(T)$ value does not change under magnetic field. This is due to the fact that at low temperature the spin polarization is complete and therefore S becomes independent of both temperature and magnetic field. For the higher Pr doped sample with $y=0.2$, similar to that of $y=0$, the $S(T)$ value also decreases under the application of magnetic field down to T_p. But below T_p, $S(T)$ increases under field. This behavior supports our interpretation of the $S(T)$ behavior of the Pr containing samples $(y<0.7)$. Actually the magnetic field (below T_p) tend to expand the in-plane Mn–O bond length while reducing the out-of-plane bond length.[24] Therefore, the collective J-T distortion is further reduced, destabilizing the orbital state ordering and hence the increase in S below T_p is as expected.

IV. CONCLUSION

We have measured the temperature variation of resistivity of the $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ $[y=0.0–0.7]$ system under zero and 1.5 T magnetic field. The resistivity data below T_p can be best fitted with $\rho(T)=\rho_{0+}\rho_{2.5}T^{2.5}$ indicating the existence of carrier magnon scattering. The best-fit region decreases with increasing Pr content, which suggest phase separation mechanism. Thermopower data (Seebeck coefficient) indicate that with the increase of Pr content, mobile carrier concentration decreases. The temperature independent TEP observed at low T is due to the fact that the spins are ferromagnetically ordered in this region. For $y\geqslant 0.2$, double peaks are observed in the TEP vs temperature curve. One peak is due to the presence of A-type AFM state and an additional peak is considered to be associated with the competition between the interaction between charge carriers and orbital degrees of freedom and spin polarization. For higher Pr concentration $(y>0.6)$, a change over from the A-type AFM to the CE-type AFM occurs in the system of our present investigation. The magnetic field dependent TEP data also indicate that the field tend to expand the in plane Mn–O bond length (reducing the out-of-plane bond length) and as a consequence, the collective Jahn-Teller distortion is reduced and orbital ordering is established. Both field dependent and field independent TEP data, therefore, provide interesting information about the phase separation in CMR and related systems, in particular.

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