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# CE-type antiferromagnetic ordering and martensitic transition in Pr-substituted $La_{0.65}Ca_{0.35}MnO_3$ from magnetic and neutron diffraction studies

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**Abstract**

Mixed ferromagnetic (FM) and antiferromagnetic (AFM: A-type and CE-type) phases and anomalous lattice parameters have been observed around 50 K in $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ ($y = 0.5$–$0.65$) from neutron diffraction studies. The critical magnetic field is profoundly increased by Pr doping. Field-dependent and temperature-dependent magnetization $M(H, T)$ and the hysteresis behaviour of resistivity indicate the presence of magnetostriction and mixed magnetic phases. The step-like behaviour of $M(H)$ data around 5 K is attributed to the martensitic transition, which is found to be related to the CE-type AFM phase in the system.

## 1. Introduction

Colossal magnetoresistive (CMR) effect in rare-earth manganites has recently been the focus of intensive research interest to tailor the macroscopic response of these materials under small external stimulating forces. Moreover, the simultaneous presence of ferromagnetic metallic (FMM) and charge-order insulating (COI) regions in some of these manganites showing phase separation phenomena [1–4] also makes these materials an attractive field of current research. The subtle balance of these separated phases can be manipulated by a variety of external parameters, especially the magnetic field producing the CMR effect. Typically, the magnetic

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field induced first-order transition is rather broad [5] in CMR manganites at temperatures above 5 K. Recently, ultra-sharp magnetization ($M$) steps have also been reported at temperatures below 5 K in $Pr_{0.5-x}Ce_xCa_{0.5}MnO_3$ [6] and in $Pr_{1-x}Ca_xMnO_3$ [7] substituted with other cations at Mn [8–11] as well as at Pr sites [12]. With decreasing temperature, these materials undergo transitions from a charge-order (CO) insulator to an FMM phase. In some other studied systems [13] the mechanism behind such ultra-sharp step-like behaviour has been attributed to the relief of strain built up during the first-order martensitic phase transition (MRT) between the CO/orbital ordered (OO) antiferromagnetic (AFM)–FMM ground state during cooling. However, observation of a structural anomaly around this transition is an important criterion for supporting an MRT as such a step might also appear due to the intrinsic moment of the rare-earth ion and magnetic domain wall movement [14]. It is also true that the applied magnetic field could affect the subtle energy balance in the coexisting phases and trigger an FMM state. But according to the traditional AFM theory [15], a very high field would be required to melt the robust CO-AFM state (∼25 T at 4 K) which is not consistent with the expected step-like CO-AFM to FM transition in the $M(H)$ curve observed under low field (a few tesla) for the Mn-site substituted system [16]. Apart from these and, most importantly, the macro/microscopic basis of these steps are still a subject of debate. In order to clarify the mechanism of coexisting FM–AFM clusters, the La–Pr–Ca–Mn–O (LPCM) system with typical phase separation characteristics [17] is considered to be an ideal candidate for further investigation. The end members of the series, i.e., $LaCaMnO_3$ and $PrCaMnO_3$, have robust FMM and COI states, respectively, at low temperature. Moreover, study of the origin of ultra-sharp steps related with varying A-site concentration (tolerance factor) in LPCM is of particular interest.

In the present paper, our aim is to find the nature of magnetic ordering and to explain the step-like field-dependent magnetization observed in the phase-separated $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ system from low-temperature magnetic, transport and neutron diffraction studies. From observation of the discontinuity in the lattice volume and the presence of magnetostriction we confirm a martensitic-type transition associated to the CE-type AFM order in the present system.

## 2. Experimental details

$(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ ($y = 0.5$–$0.65$) samples were synthesized using the standard solid-state reaction method. Constituent oxides $La_2O_3$, $Pr_6O_{11}$, $CaCO_3$ and $Mn(CH_3COO)_2$, $4H_2O$ were mixed thoroughly in stoichiometric proportions and calcined initially at 800 °C for 6 h. The samples were then pelletized, and sintered at 1200 °C for 12 h. The final sintering was carried out for 12 h at high temperature (1350 °C). The resistivity of the samples was measured by the conventional four-probe method. Temperature-dependent and field-dependent magnetization ($M$) measurements were performed using a SQUID magnetometer (Quantum Design MPMS). Neutron diffraction studies were carried out on the multi PSD-based neutron powder diffractometer ($\lambda = 1.249$ Å) at Dhruva reactor in Bhabha Atomic Research Centre, Mumbai, India. The lattice parameters and hence unit cell volume ($V$) were obtained from the profile refinement of the neutron diffraction data recorded at several temperatures between 15 and 300 K.

## 3. Result and discussions

Figure 1 shows the magnetization of the LPCM system (with $y = 0.5$, 0.6 and 0.65) as a function of magnetic field. Interestingly, for $y = 0.5$, a metamagnetic transition is observed

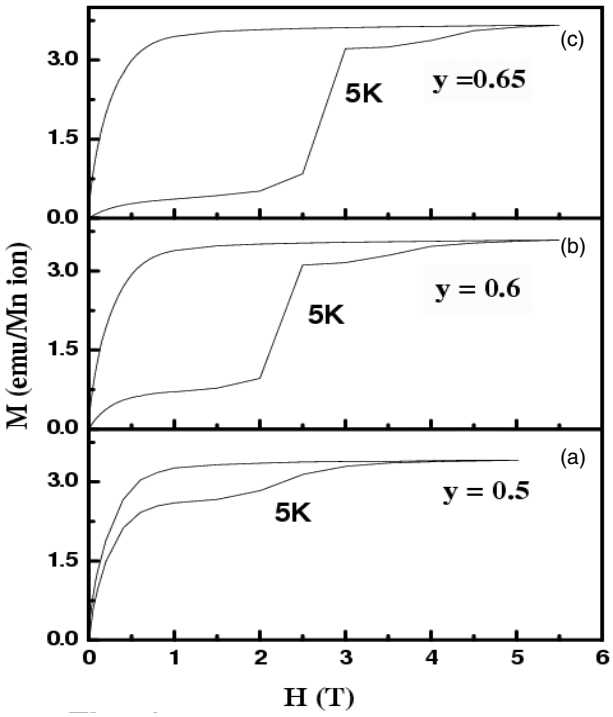


**Figure 1.** Magnetization ($M$) versus field ($H$) isotherms at 5 K for the $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ system with (a) Pr = 0.5, (b) Pr = 0.6 and (c) Pr = 0.65. With the increase of Pr content a smooth to step-like transition in $M$ value is observed for some critical DC field ($H_C$). The critical magnetic field for the first magnetization step increases with the Pr content.

below 5 K in the vicinity of a field of 1.8 T in the $M(H)$ isotherm. Similar behaviour is also observed for the samples with $y = 0.6$ and 0.65 exhibiting a metamagnetic transition near 5 K. The magnetic transition for $y = 0.5$ is broader (width ∼1 T) in contrast to those of the samples with $y = 0.6$ and 0.65 for which the said transitions are quite sharp and step-like in nature (with width ∼ 0.3 and 0.25 T, respectively). For $y = 0.6$, the critical field $H_C$ for the first magnetic step at 5 K is 2 T, whereas the corresponding $H_C$ for $y = 0.65$ is 2.5 T. At low temperature (5 K), the magnetization attains saturation ($M_S$) around ∼3.6 $\mu_B$/Mn ion for all the samples with field varying from 3 T (for $y = 0.5$) to 5 T (for $y = 0.65$). The above behaviour clearly indicates the coexistence of FM and AFM phases in the present LPCM system.

The phase separation behaviour of the samples can also be studied from the temperature-dependent $M(T)$ data. Figure 2 showing the plot of $M(T)$ data under zero-field-cooled (ZFC) and field-cooled-cooled (FCC) conditions in the presence of a magnetic field of 10 kOe within the temperature range 5–300 K. The $M(T)$ curves of the samples with $y = 0.6$ and 0.65 exhibit weak maxima around 210 K, which is a signature of the onset of CO in the system. $M_{ZFC}(T)$ data show FM transitions at ∼120, 110 and 100 K, respectively, for the samples with $y = 0.5$, 0.6 and 0.65. Below these transitions, the magnetization reaches a constant value. At around 50 K, $M_{ZFC}(T)$ shows an AFM transition for all the samples. FCC data exhibit an FM transition at ∼50 K (magnetization data have been collected during the field-cooling cycle). Below this temperature, $M(T)$ reaches a saturation value which is lower than the corresponding theoretically calculated one (∼3.7 $\mu$B). The concordance of these data implies that the metastable low-temperature state of the sample is a mixture of FM and COI

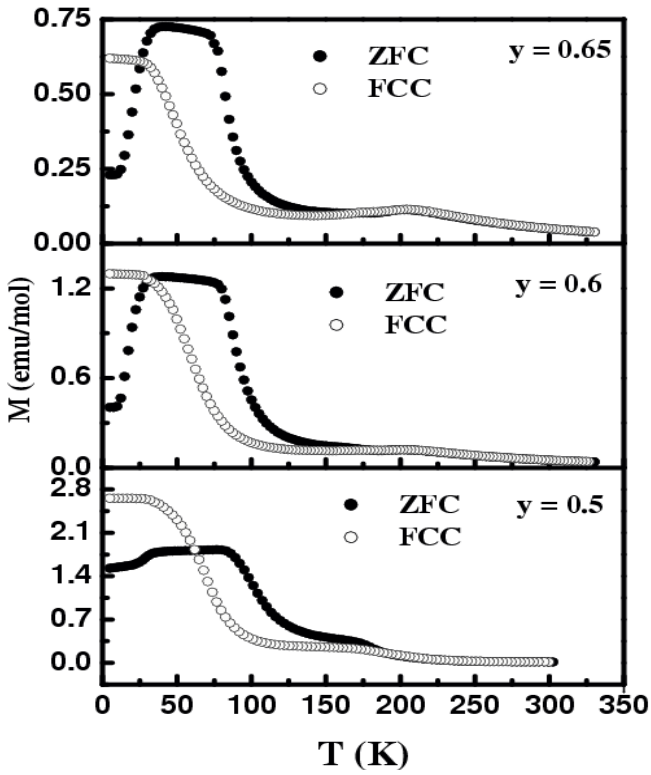


**Figure 2.** Magnetization ($M$) is plotted against temperature ($T$) for the samples in the series $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ for zero-field-cooled (ZFC) and field-cooled (FCC) processes in 10 kOe magnetic field.

antiferromagnetic regions. The most interesting feature of the $M(T)$ behaviour is that the FCC magnetization data for the $y = 0.65$ samples is (for $y = 0.6$, the maximum values of $M_{ZFC}$ and $M_{FCC}$ are almost equal) lower than those of the ZFC data, which is not trivial. However, the system with $y = 0.5$ follows the usual behaviour where the ZFC value is lower than the corresponding FCC value. The unusual behaviour shown by the samples with $y = 0.6$ and 0.65 indicate the presence of strong magnetostriction in these systems [18].

Figure 3 represents the temperature variation of the resistivity ($\rho$) of LPCM (experimental data have been taken both in heating and cooling cycles) where the $y = 0.5$ system shows a clear hysteresis behaviour. But, in the temperature range of our measurement (down to 10 K), we did not observe any such hysteresis behaviour for the sample with $y = 0.65$. During cooling, the onset of the decrease of resistivity starts with the nucleation of the FM phase at $\sim$100 K for $y = 0.5$. Further cooling converts the system more and more from the AFM to the FM state. However, the resistivity during the warming cycle does not follow the cooling path, and the metal to insulator transition is found to be strongly hysteretic. The increase of $\rho(T)$ in the transition region is again associated with more and more of the sample becoming AFM. Within the region of the resistivity curve showing hysteresis, the difference in resistivity value (hysteresis nature) at any temperature is associated with the relative fraction of coexisting phases.

It has been proposed [19] earlier that the temperature and magnetic field induced phase transitions in the Pr-doped system resembled a martensitic-like transition (MRT) due to the

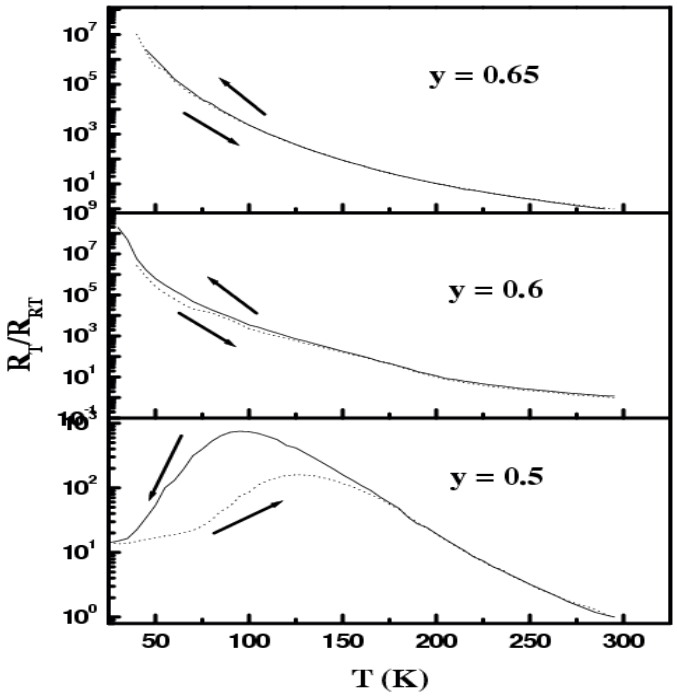


**Figure 3.** Temperature-dependent normalized resistivity (zero magnetic field) during cooling (continuous line) and heating (dashed line) cycles for the samples in the series $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}Mn$ with $y = 0.5$, 0.6 and 0.65. The hysteretic resistivity region, i.e. the difference in resistivity value at any temperature, is associated with the relative fraction of coexisting phases.

strain imposed by the different crystallographic nature of the FM and COI AFM phases [20]. However, in order to confirm if the transition is truly martensitic, anomalous behaviour of the lattice parameters at the FM–AFM transition is a necessary criterion. We performed low-temperature neutron diffraction studies at BARC (Department of Atomic Energy Facility, Mumbai, India), and the unit cell parameters were estimated. Figure 4(a) shows neutron diffraction pattern of the samples with $y = 0.5$ and 0.6. At 15 K, superlattice reflections due to AFM ordering together with ferromagnetic enhancement in the fundamental reflections were observed, indicating the mixed phase nature of the samples. In contrast to the sample with $y = 0.5$, additional AFM superlattice peaks (towards low $2\theta$ values) and some characteristic peaks (marked by C) appear in the neutron diffraction pattern of the sample with $y = 0.6$. The appearance of those additional characteristic peaks (not exhibited by the sample with $y = 0.5$) is due to Jahn–Teller distortion, which is a characteristic of charge and orbitally ordered states [21]. In the presence of charge ordering, the AFM ordering is shown to be of CE type at low temperature. In A-type spin ordering, the spins are typically ordered ferromagnetically in the $ab$ plane with the moments pointing toward the $a$ axis, and the FM planes are stacked antiferromagnetically along the $c$ axis. The CE-type spin ordering is characterized by the alternate ordering of the $Mn^{3+}$ and $Mn^{4+}$ ions. The spin ordering pattern in the $ab$ plane is rather complicated, and these planes stack antiferromagnetically along the $c$ axis. To clarify the magnetic structure of the two present samples, diffraction data of both the samples were refined using the FullProf program [22]. The superlattice reflections could be fitted to the appropriate

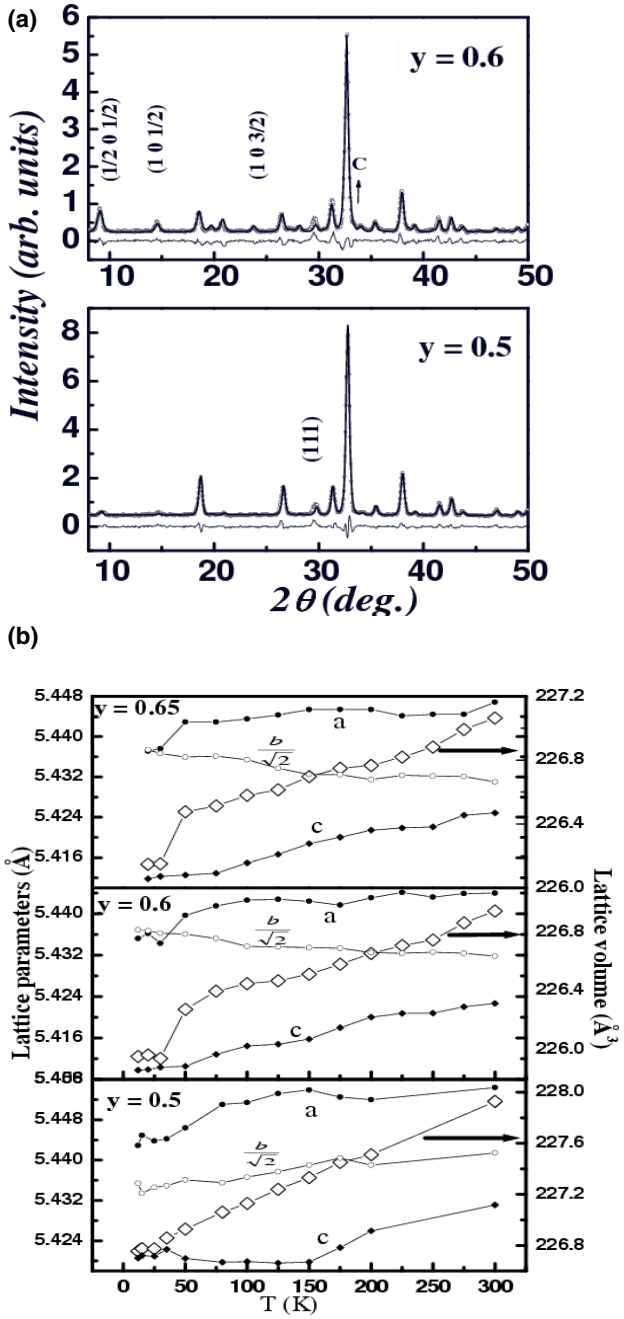


**Figure 4.** (a) Neutron diffraction patterns: observed (solid line) and calculated (open circles) for the $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ compounds with $y = 0.5$, and 0.6 recorded at 15 K. The difference between the observed and calculated patterns is shown at the bottom of each diagram. Reflections corresponding to the charge and orbital ordering are marked by C. (b) Variation of the unit cell parameters and lattice volume as a function of temperature obtained from neutron diffraction data analysis for $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ with $y = 0.5$, 0.6 and 0.65. The drastic variation of the lattice volume associated with the martensitic transition around 50 K indicates the change in strain between AFM and FM regions.

AFM structure as proposed by Wollen and Kohler [23]. For the system with $y = 0.5$, A-type antiferromagnetic ordering with $d_{x^2-y^2}$ orbital ordering sets in at low temperature with *Imma* (magnetic phase) symmetry. However, the neutron data for the sample with $y = 0.6$ are found to be fitted well by choosing a magnetic cell similar to that reported in the case of the CE-type antiferromagnetic order observed system $La_{0.5}Ca_{0.5}MnO_3$ [24] with $d_{z^2}$ orbital ordering. The characteristic strong reflections indicating CE-type structure are shown in figure 4(a). The CE-type AFM phase observed for the sample $y = 0.6$ also persists for $y = 0.65$. Moreover, the temperature variation of lattice parameters and the corresponding lattice volumes ($V$) for the samples with $y = 0.6$ and 0.65 exhibit striking anomalous behaviour around 50 K (figure 4(b)) at which AFM ordering was also observed from the $M(T)$ data, as discussed above. The sudden jump in the $V$–$T$ curve (figure 4(b)) for the samples with $y = 0.6$ and 0.65 are much sharper than that of the sample with $y = 0.5$. Moreover, for $y = 0.5$, the step in the $M(H)$ curve is smooth, whereas for $y = 0.6$ and 0.65, the steps are sharper, which is consistent with figure 4(b). From the $M(T)$ results one can also find strong evidence of the magnetostriction effect in the present system with $y = 0.6$ and 0.65. Therefore, such a drastic variation of the lattice volume occurring at 50 K is associated with the change in lattice strain between AFM and FM regions. It is obvious from the above results that, for $y = 0.5$, the AFM region is less compared to those of the $y = 0.6$ and 0.65 samples. All the above results support the observed steps in the $M(H)$ data as well as the resistivity anomaly around the same temperature ($\sim$50 K) being due to the MRT. Here it is worth mentioning that for the system where there is A-type AFM ordering ($y = 0.5$), step-like behaviour is absent, but the systems with $y = 0.6$ and 0.65, where the CE-type AFM phase is present, step-like character in the field-dependent magnetization behaviour is favoured. This might give an indication of the microscopic origin of the step-like transition in the system with CE-type AFM. Since magnetic field tends to reduce the Jahn–Teller distortion of the AFM phase, the orbital ordering is destabilized by the application of the magnetic field. As a result, the spins are reoriented with simultaneous delocalization of the carriers and, therefore, magnetization jumps result. As the CE-type AFM phase is associated to the orbital ordering, the CE-type phase is more favourable for showing step-like behaviour and MRT than the corresponding A-type AFM phase in LPCM.

## 4. Summary

To summarize, a transformation from continuous to sharp metamagnetic steps in the $M(H)$ curve is exhibited with increasing Pr concentration in the $(La_{1-y}Pr_y)_{0.65}Ca_{0.35}MnO_3$ system at low temperature. The $M(T)$ data and the thermal hysteresis in resistivity indicate the coexistence of different magnetic phases (FM/AFM) and the presence of magnetostriction in this system. The observed jump around 50 K in the temperature-dependent lattice volume for the samples with $y = 0.6$ or 0.65 is associated with the change in the lattice strain between the AFM and FM regions, which is also consistent with the $M(H)$ behaviour of the samples. These results confirm that the observed step-like transition in the $M(H)$ curve is solely due to the MRT in the present LPCM system. Moreover, it is also concluded that the MRT is favoured in the CE-type AFM (not in A-type AFM) ordered phase, leading to the possible microscopic origin of this phenomenon for which further studies of the MRT with new samples would be highly encouraging.

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