Anomalous field-dependent specific heat in charge-ordered Pr$_{1-x}$Ca$_x$MnO$_3$ and La$_{0.5}$Ca$_{0.5}$MnO$_3$

V. N. Smolyaninova$^1$, Amlan Biswas$^1$, X. Zhang$^1$, K. H. Kim$^2$, Bog-Gi Kim$^2$, S-W. Cheong$^2$, and R. L. Greene$^1$

1. Department of Physics and Center for Superconductivity Research, University of Maryland, College Park, MD 20742

2. Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08854

(March 21, 2022)

We report low temperature specific heat measurements of Pr$_{1-x}$Ca$_x$MnO$_3$ ($0.3 \leq x \leq 0.5$) and La$_{0.5}$Ca$_{0.5}$MnO$_3$ with and without applied magnetic field. An excess specific heat, $C'(T)$, of non-magnetic origin associated with charge ordering is found for all the samples. A magnetic field sufficient to induce the transition from the charge-ordered state to the ferromagnetic metallic state does not completely remove the $C'$ contribution. This suggests that the charge ordering is not completely destroyed by a “melting” magnetic field. In addition, the specific heat of the Pr$_{1-x}$Ca$_x$MnO$_3$ compounds exhibit a large contribution linear in temperature ($\gamma T$) originating from magnetic and charge disorder.

PACS number(s): 75.40.Cx, 75.30.Vn, 71.30.+h, 75.50.Cc

PACS no.: 75.40.Cx, 75.30.Vn, 71.30.+h, 75.50.Cc

Charge ordering (CO), i.e. the real space ordering of Mn$^{3+}$ and Mn$^{4+}$ ions, is one of the most intriguing properties observed in hole-doped manganites. These compounds with the generalized formula RE$_{1-x}$AE$_x$MnO$_3$ (RE being a trivalent rare-earth and AE being a divalent alkaline earth element occupying the A-site in the AMnO$_3$ perovskite structure) undergo a charge-ordering transition for certain values of $x$ and the average A-site cation radius $< r_A >$. Remarkably, a modest external magnetic field can destroy the insulating CO state and produce a metallic ferromagnetic state (FMM). The $< r_A >$ determines the one-electron bandwidth W in these materials and charge ordering is observed in materials with $x = 0.5$ with small $< r_A > \sim 1.23$ Å (and consequently small W).

Among these, Pr$_{1-x}$Ca$_x$MnO$_3$ ($< r_A > \sim 1.18$ Å) is especially interesting. This compound is a paramagnetic insulator at high temperature which undergoes a CO transition at $T_{CO} \sim 230$ K for the composition range $0.3 \leq x \leq 0.5$. An antiferromagnetic (AFM) ordering occurs below $T_{CO}$ with Neel temperature ($T_N$) changing from $\sim 180$ K ($x = 0.5$) to $\sim 140$ K ($x = 0.3$). The AFM ordering for charge-ordered Pr$_{1-x}$Ca$_x$MnO$_3$ is CE type for $x \approx 0.5$ and pseudo-CE type for $x \approx 0.3$. Although the FMM state is never realized for Pr$_{1-x}$Ca$_x$MnO$_3$ in zero magnetic field, a competition between the ferromagnetic (FM) metallic and AFM charge-ordered ground states leads to an increase of FM tendencies as $x$ decreases below 0.5. The magnitude of the magnetic field required to induce a transition to the FMM state decreases from 24 T for $x = 0.5$ to 4 T for $x = 0.3$. The charge ordering has been detected as a superlattice reflection in synchrotron, neutron, and electron diffraction experiments for $0.3 \leq x \leq 0.5$. They show that the charge modulation for these compositions in the CO state is 1:1 as observed in La$_{0.5}$Ca$_{0.5}$MnO$_3$ and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. These observations illustrate the very sensitive balance between the CO and FMM phases as $x \rightarrow 0.3$ for materials with small $< r_A >$ as in Pr$_{1-x}$Ca$_x$MnO$_3$. This was clearly demonstrated in the recent work on La$_{0.33}$Pr$_{0.67}$Ca$_{0.3}$MnO$_3$. These authors showed that by changing $x$ i.e. the relative amounts of La and Pr, the ground state could be changed from an FMM state (for $x = 0$) to the CO state (for $x = 0.33$). For intermediate values of $x$, $T_C$ was lowered on increasing $x$. In fact for a range of temperatures a micron scale phase separation (PS) between FMM and CO phases, was observed. The small magnetic fields (~4 T) needed to melt the CO state in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ also brings out the delicate balance between the FMM and CO phases as $x \rightarrow 0.3$. Therefore, the pertinent questions are: (1) What is the nature of the metallic state obtained on melting the CO state by a magnetic field? (2) Is it different from the low temperature FMM state in other manganites like La$_{0.67}$Ca$_{0.33}$MnO$_3$? We expect that low temperature specific heat experiments, carrying the information about principal excitations, might provide an answer to these questions.

In this paper we report a specific heat study of the CO state in Pr$_{1-x}$Ca$_x$MnO$_3$ ($0.5 \geq x \geq 0.3$) and the FMM state obtained on “melting” this CO state with a magnetic field. Previously, we found an anomalous excess specific heat $C'$ of non-magnetic origin in the CO state of La$_{0.5}$Ca$_{0.5}$MnO$_3$. Here we find that this anomalous contribution is also present in Pr$_{1-x}$Ca$_x$MnO$_3$ ($0.3 \leq x \leq 0.5$), even in magnetic field sufficient to induce a CO insulator to FMM transition. This indicates the coexistence of metallic and CO regions (i.e. electronic phase separation). We also found that Pr$_{1-x}$Ca$_x$MnO$_3$ ($0.3 \leq x \leq 0.5$) exhibits a large linear in temperature contribution to the specific heat due to charge and magnetic disorder. This linear term is significantly reduced.
The first term in Eq. (1) is the hyperfine contribution caused by splitting of nuclear magnetic levels of Mn and Pr ions in the field of unpaired electrons, which was observed previously in the manganites [12,13]. The origin of the γT for these electrically insulating samples will be discussed later. We discovered the anomalous contribution \( C'(T) \) previously in charge-ordered \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) \((x \approx 0.5)\) [4]. The temperature dependence of this contribution corresponds to non-magnetic excitations with dispersion relation \( \epsilon = \Delta + Bq^2 \), where \( \Delta \) is an energy gap and \( q \) is a wave vector \([14]\). Since \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \) \((0.3 \leq x \leq 0.5)\) has the same charge modulation as in \( \text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) and \( \text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \) \([12,13]\), one possible origin of the \( C'(T) \) contribution is the presence of low frequency optical phonons \([12]\) corresponding to an out of phase motion of \( \text{Mn}^{3+} \) and \( \text{Mn}^{4+} \) ions in their respective planes in the structure. Another possible origin is orbital excitations \([14]\), since the CO in manganites is accompanied by an orientational ordering of the \( d_{z^2} \) orbitals of \( \text{Mn}^{3+} \). Clearly, other experiments are needed to determine the origin of the \( C'(T) \) term.

The results of fitting the data to Eq. (1) are shown in Table 1. Fits corresponding to values listed in Table 1 are shown in Fig. 1 as solid lines. The value of \( \alpha \) is larger than that reported in Ref. [12] for the Mn hyperfine term and it decreases with \( x \). This suggests that the hyperfine term is a result of contributions from Mn and Pr nuclei. However, lower temperature measurements are needed to determine more precisely the hyperfine contribution of these materials. The \( \beta T^3 \) term is larger for \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \) than for charge-ordered \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) \((x \approx 0.5)\) [4] which indicates a smaller Debye temperature and/or a larger antiferromagnetic spin-wave contribution \((\propto T^3)\) in \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \). The data for these all charge-ordered samples can be best fit without the higher-order lattice term, \( \beta_3 T^5 \). We note that values of \( \Delta \) which differ from those listed in Table 1 by \( \pm 0.2 \) meV also give a good fit with a change of the other parameters by 10-15%. This is the error limit for the fit.

To confirm that the \( C' \) contribution is present only in the CO state, we compare the specific heat of...
As was noted in previous work \cite{16,15,17}, it is difficult to fit the system and to a spin-glass behavior, which was observed in neutron scattering \cite{2} and AC susceptibility measurements \cite{8}. This spin glass behavior is a possible cause for the large values of $\gamma$ for $x = 0.3$ and $x = 0.35$ samples. A large linear in temperature contribution to the specific heat was observed in many spin glasses previously \cite{9}. Recently a large $\gamma T$ term associated with spin disorder was also found in insulating LaMnO$_{3+\delta}$ \cite{20}.

Another possible cause for the presence of the large $\gamma T$ term is charge disorder. The charge modulation in Pr$_{1-x}$Ca$_x$MnO$_3$ ($0.3 \leq x < 0.5$) is the same as for $x = 0.5$ \cite{4}, but for $x < 0.5$ there are not enough Mn$^{4+}$ ions to provide a perfect 1:1 charge ordering of Mn$^{4+}$ and Mn$^{3+}$, resulting in charge disorder for $x < 0.5$. The two level states of different charge configurations would also have a linear in temperature specific heat similar to spin glasses (or glasses \cite{21}). We believe that the spin and charge disorder is responsible for the large values of $\gamma$ for $x = 0.3$ and $x = 0.35$ samples.

Next we discuss the effect of a magnetic field. Figure 3a shows $C/T$ vs. $T^2$ for the $x = 0.35$ sample at different fields and different thermal and magnetic history. Resistivity measurements (Fig. 3a, inset) show that in a magnetic field of 8.5 T the material is in the metallic state. Magnetization measurements show that a magnetic field of 6 T is sufficient to induce a transition from the AFM CO insulating state to the FM metallic state for our $x = 0.35$ sample. We find that the specific heat of the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ sample decreases dramatically in a magnetic field of 8.5 T (Fig. 3a). Moreover, the specific heat exhibits a memory effect characteristic of the CO manganites \cite{22}. After reducing the magnetic field from 8.5 T to 2 T (while not increasing $T$ above 20 K), the sample tends to retain its smaller specific heat, while if a 2 T magnetic field is applied to the zero field cooled (ZFC) sample (not subjected previously to a magnetic field sufficient to “melt” the charge ordering), the specific heat is exactly the same as for zero field (Fig. 3a). This behavior indicates that the decrease of the specific heat in 8.5 T is associated with the “melting” of the charge

\[ \Pr_{0.5}\text{Ca}_{0.5}\text{MnO}_3 \text{ and Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3 \text{ (Fig. 2). Doping of Cr at the Mn site destroys the CO in this compound and results in a FM metallic state at low temperature} \text{.} \]

We fit the Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.97}$Cr$_{0.03}$O$_3$ data to the form $C = \alpha T^{-2} + \gamma T + \beta T^3 + \beta_5 T^5 + \delta T^{3/2}$, where $\gamma T$ is a charge carrier contribution and $\delta T^{3/2}$ is a ferromagnetic spin-wave contribution. Values of the fitting parameters are listed in Table 1. The best fit also requires $\beta T^3$ with $\beta_5 = 0.46 \pm 1 \mu\text{J/mole-K}^2$ and $\delta T^{3/2}$ is a ferromagnetic spin-wave contribution to the specific heat in FMM manganites due to its small value and the presence of the $\gamma T$ contribution. The charge carrier contribution is close to that found in other FMM manganites \cite{15,16}. The large excess specific heat in the charge-ordered Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.97}$Cr$_{0.03}$O$_3$, is very evident in Fig. 2.

We now return to the unexpected $\gamma T$ term in the specific heat of these electrically insulating samples. The inset in figure 1 shows a plot of $\gamma$ values for the different $x$. As $x$ approaches 0.3, the values of $\gamma$ become increasingly large. In fact the $\gamma$ values are much larger than observed in metallic manganites \cite{12,14,17}, where $\gamma$ values were found to be in the range 3 - 7 mJ/mole K$^2$. As $x$ changes from 0.5 to 0.3, the magnetic ordering at low temperatures changes from CE type to pseudo CE type magnetic ordering and FM correlations increase in the system \cite{13}. This leads to frustration in the spin system and to a spin-glass behavior, which was observed in neutron scattering \cite{2} and AC susceptibility measurements \cite{8}. This spin glass behavior is a possible cause for the large values of $\gamma$ for $x = 0.3$ and $x = 0.35$ samples.

![Figure 3a](image-url)  
**Figure 3a.** Specific heat of charge-ordered Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ sample in different magnetic fields: (1) diamonds - $\mu_0 H = 0$; (2) open squares - $\mu_0 H = 8.5$ T; (3) filled circles - $\mu_0 H = 2$ T (field was reduced to 2 T after application of 8.5 T field); (4) open circles - $\mu_0 H = 2$ T (zero field cooled sample). Dashed line (5) representing specific heat data of FMM Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.97}$Cr$_{0.03}$O$_3$ sample is shown for comparison. Solid line is fit to $\mu_0 H = 8.5$ T data (described in text). The inset shows the temperature dependence of the resistivity of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ in zero and 8.5 T magnetic field. (b) Specific heat of charge-ordered La$_{0.5}$Ca$_{0.5}$MnO$_3$ with and without magnetic field. Lines are fits described in text.
ordering in this system.

A comparison of specific heat of Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ in magnetic field of 8.5 T and the FMM Pr$_{0.5}$Ca$_{0.5}$Mn$_{0.97}$Cr$_{0.03}$O$_3$ sample shows that the excess specific heat, $C''$, does not disappear completely in a 8.5 T. Rather, it appears to move to a higher temperature (Fig. 3a). Since the $C''$ contribution is found only in the CO state, our data suggest that charge ordering is not destroyed completely by 8.5 T magnetic field. This result is surprising, since the resistivity and magnetization indicate that the CO is “melted”, yielding a metallic FM state. However, our results agree with neutron scattering studies [2] that suggest coexistence of metallic and CO phases in a magnetic field. Our results are even more striking for La$_{0.5}$Ca$_{0.5}$MnO$_3$ in a “melting” magnetic field of 14 T (Fig. 3b and Table 1). Although a small $\gamma T$ term appears in this field indicating the presence of charge carriers, the $C''$ term remains essentially the same. These results indicate a coexistence of FMM and CO phases, an electronic phase separation, in a field above the “melting” magnetic field. In addition, since Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ is in the FM state at 8.5 T, the presence of the $C''$ contribution in our 8.5 T data confirms that $C''$ is not of AFM origin, as proposed in Ref. [4].

The lattice, charge carrier, hyperfine, FM spin wave and $C''$ terms were included in the fit of the magnetic field data. The fitting results are listed in Table 1. The variation of the fitting parameters within 5% of the cited values could still lead to a reasonable fit, but larger variations of these parameters lead to considerable deviations from the experimental data. 

As we discussed above, the magnetic state of Pr$_{1-x}$Ca$_x$MnO$_3$ becomes more disordered as $x$ decreases towards 0.3 and exhibits spin glass behavior. We expect the magnetic disorder to be reduced when a magnetic field induces a transition to the FMM (well ordered) state. Indeed, we observe a large decrease of $\gamma$ in a magnetic field of 8.5 T (Fig. 3, Table 1) to a value found for metallic manganites [2, 10-13]. The change in magnetic state appears to have removed (at least partially) the magnetic disorder responsible for the anomalously large $\gamma T$ term in insulating Pr$_{0.65}$Ca$_{0.35}$MnO$_3$. However, it is not possible to determine what part of the $\gamma T$ term found at 8.5 T corresponds to the charge carrier contribution since some magnetic disordere may remain.

The $\beta$ value, 0.12 ± 0.01 mJ/mole-K$^2$, is close to the $\beta$ value found in metallic manganites. This decrease of $\beta$ in magnetic field is likely due to two effects: the absence of the AFM spin-wave contribution $\beta_{AFM} T^3$ at this magnetic field and the decrease of the lattice contribution $\beta_{lat} T^3$ due to the decrease of the unit cell volume at the “melting” field [23]. The 8.5 T data fit well without including a FM spin-wave contribution. The change of the specific heat in the FMM state (difference between data sets (3) and (2) in Fig. 3) does not correspond to a temperature and magnetic field dependence of FM spin-waves, indicating, that other contributions to $C$ are also changing in the magnetic field. This does not permit us to resolve a FM spin-wave contribution from our data.

We have shown that an anomalous $C''$ term is observed for the composition range studied (0.3 < $x$ < 0.5). These results support our view that this contribution caused by low frequency excitations due to the arrangement of the Mn$^{+3}$ and Mn$^{+4}$ ions in separate sublattices in the CO state. TEM studies have shown that the charge modulation in the CO state for 0.3 < $x$ < 0.5 is 1:1, i.e. the same as in the $x = 0.5$ compound. This is supported by the observation that the gap value in the $C''$ excitation spectrum is similar for all the compounds studied here.

In conclusion, we have found a large linear in $T$ term in the low temperature specific heat of Pr$_{1-x}$Ca$_x$MnO$_3$ as $x$ approaches the AFM-FM boundary of the phase diagram. This contribution is most likely associated with spin and charge disorder. In the FM state induced by a magnetic field the $\gamma T$ contribution decreases to the typical value for metallic manganites. We found that Pr$_{1-x}$Ca$_x$MnO$_3$ (0.3 < $x$ < 0.5) compounds, which have the same type of the charge ordering as La$_{1-x}$Ca$_x$MnO$_3$ ($x \approx 0.5$), have an excess specific heat, $C''$, of non-magnetic origin. A magnetic field sufficient to induce the transition from the insulating AFM to the metallic FM state in the Pr$_{0.65}$Ca$_{0.35}$MnO$_3$ and La$_{0.5}$Ca$_{0.5}$MnO$_3$ compounds modifies, but does not eliminate the $C''$ contribution. This suggest that charge ordering is not completely destroyed by the “melting” magnetic field and CO and metallic regions coexist in the sample.

Acknowledgment: We thank A. J. Millis for helpful discussion, H. D. Drew, J. Cerne, M. Grayson, J. Simpson, G. Jenkins and D. Schmadel for use of 14 T magnet. This work is supported in part by the NSF-MRSEC at Maryland, NSF-DMR-9802513 at Rutgers.

[1] Z. Jiráš et al., J. Magn. Magn. Mat. 53, 153 (1985).
[2] H. Yoshizawa et al., Phys. Rev. B 52, R13145 (1995).
[3] Y. Tomioka et al., Phys. Rev. B 53, R1689 (1996).
[4] D. E. Cox et al., Phys. Rev. B 57, 3305 (1998).
[5] M. Tokunaga et al., Phys. Rev. B 55, 5259 (1995).
[6] S. Mori et al., Phys. Rev. B 59, 13573 (1999).
[7] C. H. Chen and S-W. Cheong, Phys. Rev. Lett. 76, 4042 (1996).
[8] P. G. Radaelli et al., Phys. Rev. B 55, 3015 (1997).
[9] M. Uehara et al., Nature 399, 560 (1999).
[10] T. Katsufuji et al., J. Phys. Soc. Jpn. 68, 1090 (1999).
[11] E. S. R. Gopal, Specific Heats at Low Temperatures, Plenum Press, New York (1966).
[12] B. F. Woodfield et al., Phys. Rev. Lett. 78, 3201 (1997).
[13] J. E. Gordon et al., Phys. Rev. B 59, 127 (1999).
[14] V. N. Smolyaninova et al., Phys. Rev. B 58, R14 725 (1998).
[15] M. R. Lees et al., Phys. Rev. B 59, 1298 (1999).
[16] J. J. Hamilton et al., Phys. Rev. B 54, 14 926 (1996).
TABLE I. Summary of the fitting results for the specific heat data. The units of different quantities are: $\alpha$ (mJ-K/mole), $\gamma$ (mJ/mole-K$^2$), $\beta$ (mJ/mole-K$^4$), $\Delta$ (meV), and $B$ (meV-A$^2$).

| $x$ (Pr$_{1-x}$Ca$_x$MnO$_3$) | $\alpha$ | $\gamma$ | $\beta$ | $\Delta$ | $B$ |
|-----------------------------|---------|---------|---------|---------|-----|
| 0.3                         | 63      | 30.6    | 0.30    | 1.73    | 12.2|
| 0.35                        | 56      | 15.7    | 0.39    | 1.15    | 20.7|
| 0.45                        | 28      | 3.1     | 0.31    | 1.15    | 24.2|
| 0.5 (0% Cr)                 | 22      | 2.4     | 0.26    | 1.15    | 23.7|
| 0.5 (3% Cr)                 | 26      | 0.5     | 0.22    |         |     |
| 0.35 ($\mu_0H = 8.5$ T)     | 66      | 7.0     | 0.12    | 3.46    | 7.6 |
| La$_{0.5}$Ca$_{0.5}$MnO$_3$ ($\mu_0H = 0$) | 0.14 | 0.72    | 17      |
| La$_{0.5}$Ca$_{0.5}$MnO$_3$ ($\mu_0H = 14$ T) | 2.2 | 0.11 | 0.72 | 16.9 |