

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

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. Greene¹

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

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

(Received 11 April 2000)

We report low temperature specific heat measurements of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$) and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with and without applied magnetic field. An excess specific heat, $C'(T)$, of nonmagnetic 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 $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds exhibit a large contribution linear in temperature (γT) originating from magnetic and charge disorder.

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 $R_{1-x}M_x\text{MnO}_3$ (R being a trivalent rare-earth and M being a divalent alkaline earth element occupying the A site in the $A\text{MnO}_3$ perovskite structure) undergo a charge-ordering transition for certain values of x and the average A -site cation radius $\langle r_A \rangle$. Remarkably, a modest external magnetic field can destroy the insulating CO state and produce a metallic ferromagnetic state (FMM). The $\langle r_A \rangle$ determines the one-electron bandwidth W in these materials and charge ordering is observed in materials with $x = 0.5$ with small $\langle r_A \rangle \sim 1.23 \text{ \AA}$ (and consequently small W).

Among these, $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($\langle r_A \rangle \sim 1.18 \text{ \AA}$) is especially interesting. This compound is a paramagnetic insulator at high temperature which undergoes a CO transition at $T_{\text{CO}} \sim 230 \text{ K}$ for the composition range $0.3 \leq x \leq 0.5$. An antiferromagnetic (AFM) ordering occurs below T_{CO} with Néel temperature (T_N) changing from $\sim 180 \text{ K}$ ($x = 0.5$) to $\sim 140 \text{ K}$ ($x = 0.3$).¹⁻³ The AFM ordering for charge-ordered $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ is CE type for $x \approx 0.5$,¹ and pseudo-CE type for $x \approx 0.3$.^{1,2,4} Although the FMM state is never realized for $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ 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 $x = 0.5$,⁵ to 4 T for $x = 0.3$.² The charge ordering has been detected as a superlattice reflection in synchrotron,⁴ neutron,^{1,2} and electron diffraction⁶ 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 $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (Refs. 7 and 8) and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$.⁶ These observations illustrate the very sensitive balance between the CO and FMM phases as $x \rightarrow 0.3$ for materials with small $\langle r_A \rangle$ as in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$. This was clearly demonstrated in the recent work on $\text{La}_{5/8-x}\text{Pr}_x\text{Ca}_{3/8}\text{MnO}_3$.⁹ 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 $x = \frac{5}{8}$). For intermediate values of x , the Curie temperature (T_C) was lowered

on increasing x . In fact, for a range of temperatures, a micron scale phase separation between FMM and CO phases was observed.⁹ The small magnetic fields ($\sim 4 \text{ T}$) needed to melt the CO state in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ also brings out the delicate balance between the FMM and CO phases as $x \rightarrow 0.3$. Therefore, the pertinent questions are: (i) What is the nature of the metallic state obtained on melting the CO state by a magnetic field? (ii) Is it different from the low temperature FMM state in other manganites like $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$? 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 $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.5 \geq x \geq 0.3$) and the FMM state obtained on ‘melting’ this CO state with a magnetic field. Previously, we found an anomalous excess specific heat C' of nonmagnetic origin in the CO state of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Here we find that this anomalous contribution is also present in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$), even in a 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 $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$) exhibits a large linear in temperature contribution to the specific heat due to charge and magnetic disorder. This linear term is significantly reduced upon the application of the magnetic field due to reduction of the disorder.

For this study we used ceramic samples of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.3, 0.35, \text{ and } 0.45$), $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$, and a single crystal of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Ceramic samples were prepared by a standard solid state reaction technique (details are described in Ref. 10). X-ray powder diffraction showed that all samples are single phase and good quality. The single crystal was grown by the floating zone technique. The specific heat was measured in the temperature range 2–17 K and magnetic field range 0–8.5 T by relaxation calorimetry. This method has a relative accuracy of $\pm 3\%$. Magnetization was measured with a commercial SQUID magnetometer, and resistivity was measured by a standard four-probe technique.

Figure 1 shows the low temperature specific heat of the $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ system plotted as C/T vs T^2 , for different

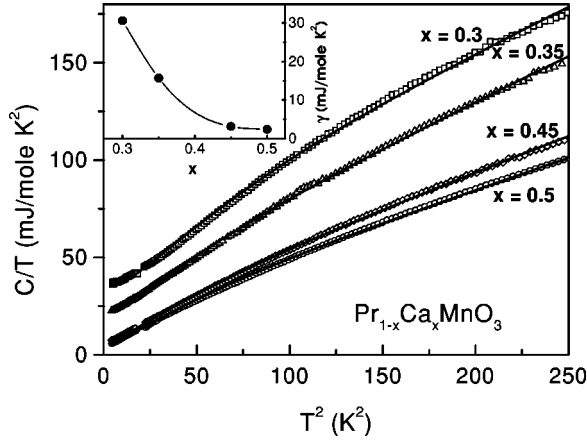


FIG. 1. Specific heat of $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ samples plotted as C/T vs T^2 . Lines are fits described in text. Inset shows γ values for different concentrations x (solid line is a guide to the eye).

values of x in the temperature range from 2 to 16 K. Two anomalous contributions are evident from these data: an excess specific heat (indicated by the nonlinearity of the C/T vs T^2 plot) and the presence of a large γT term in insulating $x=0.3$ and 0.35 compositions. The low temperature specific heat $C(T)$ of an AFM insulator should be βT^3 , because both lattice and AFM spin-wave contributions are proportional to T^3 ,¹¹ which should be a straight line passing through the origin in the C/T vs T^2 plot. This is not the case for any of our samples. Therefore, we express the low temperature specific heat of our samples in the following form:

$$C = \alpha T^{-2} + \gamma T + \beta T^3 + C'(T). \quad (1)$$

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 $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \approx 0.5$).¹⁴ The temperature dependence of this contribution corresponds to nonmagnetic excitations with dispersion relation $\epsilon = \Delta + Bq^2$, where Δ 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 $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$,^{1,2,4,6} one possible origin of the $C'(T)$ contribution is the presence of low frequency optical phonons¹⁴ corresponding to an out of phase motion of Mn^{3+} and 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 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 I. Fits corresponding to values listed in Table I are shown in Fig. 1 as solid lines. The value of α 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 βT^3 term is larger for $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ than for charge-

TABLE I. Summary of the fitting results for the specific heat data. The units of different quantities are α (mJ K/mole), γ (mJ/mole K²), β (mJ/mole K⁴), Δ (meV), and B (meV Å²).

x ($\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$)	α	γ	β	Δ	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	6.5	0.22		
0.35 ($\mu_0 H = 8.5$ T)	66	7.0	0.12	3.46	7.6
$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($\mu_0 H = 0$)			0.14	0.72	17
$\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ ($\mu_0 H = 14$ T)		2.2	0.11	0.72	16.9

ordered $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \approx 0.5$),¹⁴ 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 all these charge-ordered samples can be best fit without the higher-order lattice term, $\beta_5 T^5$. We note that values of Δ which differ from those listed in Table I by ± 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 $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$ (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.¹⁰ We fit the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$ data to the form $C = \alpha T^{-2} + \gamma T + \beta T^3 + \beta_5 T^5 + \delta T^{3/2}$, where γT 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 I. The best fit also requires $\beta_5 T^5$ with $\beta_5 = 0.46 \pm 1 \mu\text{J/mole K}^6$ and $\delta = 0$. As was noted in previous work,^{16,15,17} it is difficult to resolve the ferromagnetic spin-wave contribution to the specific heat in FMM manganites due to its small value and the presence of the γT contribution. The charge carrier contribution is close to that found in other FMM manganites.^{15,16} The large excess specific heat in the charge-ordered

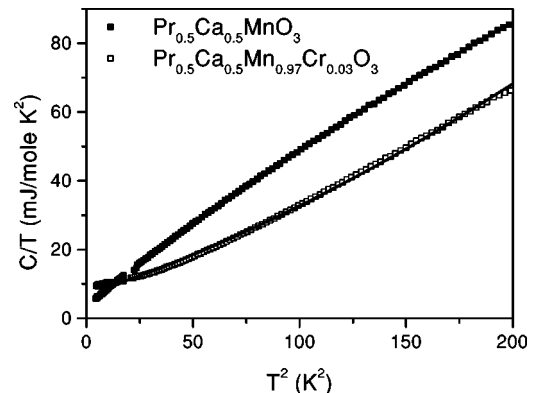


FIG. 2. Specific heat of charge-ordered $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and ferromagnetic metallic $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$ samples plotted as C/T vs T^2 . Line is fit described in text.

$\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ sample compared to the FMM $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$, is very evident in Fig. 2.

We now return to the unexpected γT term in the specific heat of these electrically insulating samples. The inset in Fig. 1 shows a plot of γ values for the different x . As x approaches 0.3, the values of γ become increasingly large. In fact, the γ values are much larger than those observed in metallic manganites,^{12,15–17} where γ 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.^{1,2} This leads to frustration in the spin system and to a spin-glass behavior, which was observed in neutron scattering² and ac susceptibility measurements.¹⁸ This spin glass behavior is a possible cause for the large values of γ 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.¹⁹ Recently, a large γT term associated with spin disorder was also found in insulating $\text{LaMnO}_{3+\delta}$.²⁰

Another possible cause for the presence of the large γT term is charge disorder. The charge modulation in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x < 0.5$) is the same as for $x=0.5$,² 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 glasses²¹). We believe that the spin and charge disorder is responsible for the large values of γ for $x=0.3$ and $x=0.35$ samples.

Next we discuss the effect of a magnetic field. Figure 3(a) shows C/T vs T^2 for the $x=0.35$ sample at different fields and different thermal and magnetic history. Resistivity measurements [Fig. 3(a), 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 $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ sample decreases dramatically in a magnetic field of 8.5 T [Fig. 3(a)]. Moreover, the specific heat exhibits a memory effect characteristic of the CO manganites.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. 3(a)]. This behavior indicates that the decrease of the specific heat in 8.5 T is associated with the “melting” of the charge ordering in this system.

A comparison of specific heat of $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ in a magnetic field of 8.5 T and the FMM $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$ 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. 3(a)]. Since the C' contribution is found only in the CO state, our data suggest that charge ordering is not destroyed completely by a 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

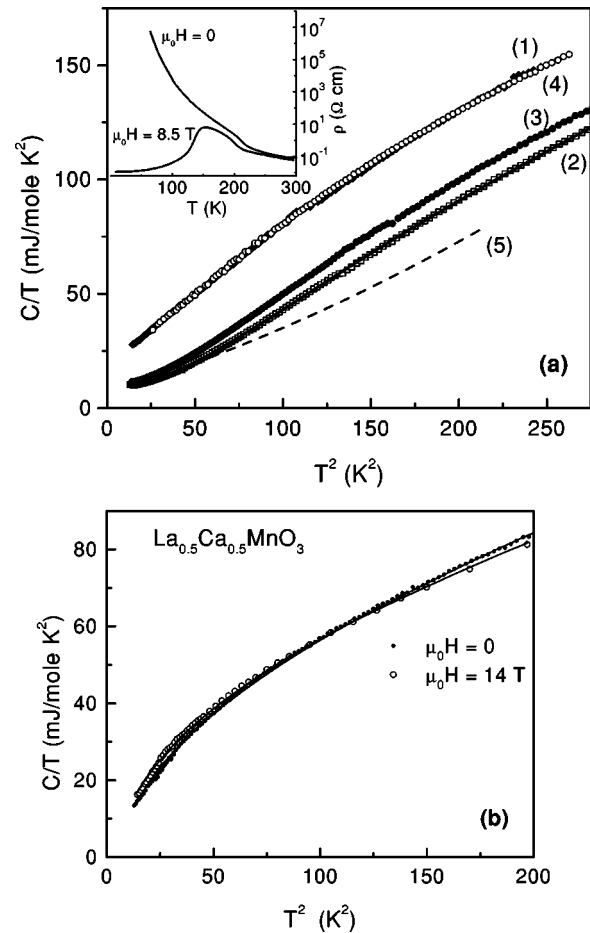


FIG. 3. (a) Specific heat of charge-ordered $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ sample in different magnetic fields: (1) diamonds: $\mu_0 H=0$; (2) open squares: $\mu_0 H=8.5$ T; (3) filled circles: $\mu_0 H=2$ T (field was reduced to 2 T after application of 8.5 T field); (4) open circles: $\mu_0 H=2$ T (zero field cooled sample). Dashed line (5) representing specific heat data of FMM $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$ 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 $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ in zero and 8.5 T magnetic field. (b) Specific heat of charge-ordered $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with and without magnetic field. Lines are fits described in text.

results agree with neutron scattering studies² that suggest coexistence of metallic and CO phases in a magnetic field. Our results are even more striking for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ in a “melting” magnetic field of 14 T [Fig. 3(b) and Table I]. Although a small γT 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 $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ 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. 15.

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 I. 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 $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ 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 γ in a magnetic field of 8.5 T (Fig. 3, Table I) to a value found for metallic manganites.^{12,16,15,17} The change in magnetic state appears to have removed (at least partially) the magnetic disorder responsible for the anomalously large γT term in insulating $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$. However, it is not possible to determine what part of the γT term found at 8.5 T corresponds to the charge carrier contribution since some magnetic disorder may remain.

The β value, 0.12 ± 0.01 mJ/mole K^4 , is close to the β value found in metallic manganites. This decrease of β in magnetic field is likely due to two effects: the absence of the AFM spin-wave contribution $\beta_{\text{AFM}}T^3$ at this magnetic field and the decrease of the lattice contribution $\beta_{\text{lat}}T^3$ 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 re-

sults support our view that this contribution is 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 $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ 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 γT contribution decreases to the typical value for metallic manganites. We found that $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.3 \leq x \leq 0.5$) compounds, which have the same type of the charge ordering as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x \approx 0.5$), have an excess specific heat, C' , of nonmagnetic origin. A magnetic field sufficient to induce the transition from the insulating AFM to the metallic FM state in the $\text{Pr}_{0.65}\text{Ca}_{0.35}\text{MnO}_3$ and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ compounds modifies, but does not eliminate the C' contribution. This suggests that charge ordering is not completely destroyed by the “melting” magnetic field, and CO and metallic regions coexist in the sample.

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

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