Specific heat of $Pr_{0.6}(Ca_{1-x}Sr_x)_{0.4}MnO_3$ ($0 \leq x \leq 1$)

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We present the results of a specific heat study of the $Pr_{0.6}(Ca_{1-x}Sr_x)_{0.4}MnO_3$ ($0 \leq x \leq 1$) manganite system as a function of doping concentration $x$ and temperature. The low-temperature specific heat data indicate that these materials have Debye temperatures of 333–344 K and reveal the presence of a $1/T^2$ hyperfine term. For $x \geq 0.25$ the samples are metallic ferromagnets at low temperature with $\gamma$ values of 4.5–5.7 mJ/mol K$^2$. However, no $T^3$ term associated with the presence of ferromagnetic spin waves can be resolved in the data. As $x$ decreases below $x = 0.25$, the materials become increasingly insulating in character and antiferromagnetic order is preferred. The $x = 0.0$ sample is an antiferromagnetic charge ordered insulator. In this doping regime, the low-temperature specific heat contains an additional contribution which is attributed to the presence of antiferromagnetic spin waves. The high-temperature specific heat data clearly show the onset of the charge and magnetic ordering. The entropy loss accompanying the magnetic transition in each of these materials is much smaller than expected. This discrepancy is attributed to a combination of factors, including the localization of magnetic ordering. The entropy loss accompanying the magnetic transition in each of these materials is much smaller than expected. This discrepancy is attributed to a combination of factors, including the localization of magnetic ordering.

I. INTRODUCTION

Distorted manganese perovskites with the composition $R_{1-x}A_xMnO_3$, where $R$ is a trivalent rare earth and $A$ is a divalent alkali earth, have recently been the focus of a large number of experimental and theoretical studies because they exhibit a range of extraordinary magnetic, electronic, and structural properties including colossal negative magnetoresistance, charge ordering, and magnetic field induced changes in structure. Despite the surge of interest in these materials there have been relatively few reports on the specific heat of the doped manganites. There have been some high-temperature specific heat measurements of $La_{1-x}Ca_xMnO_3$ (Refs. 4–6) and $Nd_{1-x}Sr_xMnO_3$ (Ref. 7) around the ferromagnetic and charge ordering transitions. Some data have also been presented on studies of the low temperature specific heat of $Nd_{1-x}Sr_xMnO_3$, $La_{1-x}Sr_xMnO_3$, and $La_{1-x}A_xMnO_3$ with $A = Ba$ at $x = 0.33$ and $A = Ca$ at $x = 0.2$ (Ref. 9) and $A = Ca$, $Sr$, and $Ba$ with $x$ fixed at 0.3.10

In this paper we examine the temperature dependence of the specific heat $C(T)$ of some $Pr_{0.6}(Ca_{1-x}Sr_x)_{0.4}MnO_3$ ($0 \leq x \leq 1$) samples. Although the level of alkaline earth doping remains constant throughout this series, the two end compounds show very different properties. $Pr_{0.6}Ca_{0.4}MnO_3$ undergoes a charge ordering (CO) transition at 250 K and orders antiferromagnetically (AFM) at 160 K. In zero magnetic field the resistivity $\rho$ of this material increases with decreasing temperature; at low temperature the compound becomes an insulator. The application of a sufficiently intense magnetic field at temperatures below 250 K produces a metamagnetic transition into a ferromagnetically ordered state. This transition is accompanied by a switch to a high conductivity state. At low temperature the field induced decrease in $\rho$ can be described as an insulator-metal transition.11–14 Replacement of $Ca$ with $Sr$ changes the degree of distortion present within the structure and drives the system towards a ferromagnetically ordered state. For $0.15 \leq x \leq 0.25$ there is a coexistence of AFM and ferromagnetic (FM) ordering. For $0.25 \leq x \leq 1.0$ the system is FM and there is a rapid increase in the Curie temperature $T_C$ with $x$.15 The end compound $Pr_{0.6}Sr_{0.4}MnO_3$ has a Curie temperature $T_C$ of 305 K. Above $T_C$, $\rho$ has an activated temperature dependence, while below $T_C$, the resistivity falls with decreasing temperature. A large negative magnetoresistance is observed at temperatures around $T_C$.15,16 At 105 K, $Pr_{0.6}Sr_{0.4}MnO_3$ undergoes a distortion from a high-temperature orthorhombic $Pnma$ to a low-temperature monoclinic $I2/a$ structure.17 This means that measuring the specific heat capacity of the $Pr_{0.6}(Ca_{1-x}Sr_x)_{0.4}MnO_3$ system provides us with a good opportunity to study a number of the phenomena exhibited by manganite materials, while minimizing the changes in the lattice contribution to the specific heat, which in turn should make the interpretation of the data more straightforward.

II. EXPERIMENTAL DETAILS

Polycrystalline samples of $Pr_{0.6}(Ca_{1-x}Sr_x)_{0.4}MnO_3$ ($0 \leq x \leq 1$) were prepared from stoichiometric quantities of $Pr_5O_{11}$, $CaCO_3$, $SrCO_3$, and $MnO_2$. The starting materials were mixed and fired for 12 h at 1200 $^\circ$C, then reground, compressed into pellets and heated to 1350 $^\circ$C for 24 h. X-ray analysis revealed all the samples to be single phase. The specific heat measurements were made in the temperature range 2 to 20 K using a standard heat pulse-relaxation method and from 20 to 305 K using an adiabatic technique. In both experimental set up, the data were collected while warming the sample. Magnetization versus temperature ($M v T$) and magnetization versus applied field ($M v H$) curves were obtained using a Quantum Design MPMS5 SQUID magnetometer.
The specific heat of samples of La$_{1-x}$Sr$_x$MnO$_3$ down to 300 mK and observed a clear increase in $C(T)$ at low temperature. Writing

$$
\alpha = \frac{R}{3} \left( \frac{I}{T} \right) \left( \frac{\mu_I H_{hyp}}{k_B} \right)^2
$$

where $I$ is the nuclear spin = 5/2 for Mn$^{55}$ and $\mu_I$ is the nuclear magneton we can calculate the field strength $H_{hyp}$ at the Mn site. 18 We obtain values of around $7 \times 10^7$ A/m (see Table II). The hyperfine term decreases only slightly as the Sr content $x$ increases. In these materials the shifting of the nuclear Schottky anomaly to reasonably high temperatures by the Hund’s rules alignment of electron spins, coupled with the fact that $^{16}$O carries no nuclear moment, should allow the determination of the local magnetic field at the Mn sites and provides a means of discerning where the doped carriers are residing. 8 In this case, the small variations in $H_{hyp}$ indicate a nearly constant number of holes at the Mn sites, which is consistent with the constant level of alkali earth doping in these materials.

Secondly we find that the $\gamma$ values all lie in the range 4.5—5.7 mJ/mol K$^2$ (see Table I). These values are in line with previous work on similar materials. For example, $\gamma$ values from 4.4—6.1 mJ/mol K$^2$ have been reported for La$_{0.7}$Ba$_{0.3}$MnO$_3$, 5.2—7.8 mJ/mol K$^2$ for La$_{1-x}$Ca$_x$MnO$_3$ with $0.2 < x < 0.33$, and 6.0 mJ/mol K$^2$ for La$_{0.7}$Sr$_{0.3}$MnO$_3$. 5,9,10 In another study of La$_{1-x}$Sr$_x$MnO$_3$, the inclusion of a hyperfine and $T^{3/2}$ magnetic term in the fitting process produced slightly lower $\gamma$ values of 3—3.5

### Table I. Summary of the fitting results for the specific heat versus temperature data shown Fig. 1 for samples with the composition Pr$_{0.6}$(Ca$_{1-x}$Sr$_x$)$_{0.4}$MnO$_3$ ($0 \leq x \leq 1$). The definitions of the coefficients are given in the text. The units are all mJ/mol K$^{n+1}$ where $n$ is the subscript given next to the fitting coefficient.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\alpha_{-2}$</th>
<th>$\gamma \times 10^3$</th>
<th>$\beta_2 \times 10^4$</th>
<th>$\beta_3 \times 10^7$</th>
<th>$\delta \times 10^3$</th>
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<tr>
<td>0.0</td>
<td>28.0</td>
<td>5.50</td>
<td>0.84</td>
<td>1.89</td>
<td>($n = 2$)</td>
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<tr>
<td>0.25</td>
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<td>4.72</td>
<td>2.38</td>
<td>11.54</td>
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<tr>
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<td>4.51</td>
<td>2.41</td>
<td>10.06</td>
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</tr>
<tr>
<td>0.75</td>
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<td>2.62</td>
<td>6.76</td>
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</tr>
<tr>
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<td>2.50</td>
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</tr>
</tbody>
</table>

$^a$See Ref. 15.
$^b$Calculated from $\beta_3$.
$^c$Calculated from high-temperature data.

### Table II. Physical parameters for samples of composition Pr$_{0.6}$(Ca$_{1-x}$Sr$_x$)$_{0.4}$MnO$_3$ ($0 \leq x \leq 1$) extracted from both the low- and the high-temperature heat capacity data.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$T_C$ $^a$ (K)</th>
<th>$H_{hyp}$ $^b$ ($\times 10^7$/A/m)</th>
<th>$\theta_D$ $^b$ (K)</th>
<th>$\theta_B$ $^c$ (K)</th>
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<tr>
<td>0.0</td>
<td>$T_C = 160$ K</td>
<td>5.34</td>
<td>433</td>
<td></td>
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<tr>
<td>0.5</td>
<td>196</td>
<td>7.76</td>
<td>344</td>
<td>432</td>
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<tr>
<td>0.75</td>
<td>235</td>
<td>7.64</td>
<td>342</td>
<td>426</td>
</tr>
<tr>
<td>1.0</td>
<td>350</td>
<td>6.45</td>
<td>333</td>
<td>429</td>
</tr>
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$^a$See Ref. 15.
$^b$Calculated from $\beta_3$.
$^c$Calculated from high-temperature data.
mJ/mole K². Tc increases with Sr content from 196 to 305 K but there is no clear correlation between the value of γ and Tc. Note that in the double exchange (DE) model, Tc is proportional to the effective transfer integral t for electrons hopping between Mn ions. In the tight binding approximation N(EF), the density of states at the Fermi energy, is inversely proportional to t. So we may expect γ to decrease with Tc. All the Sr rich samples in this study (x ≥ 0.25) exhibit a low-temperature resistivity which decreases with decreasing temperature. Assuming a linear term in the specific heat arises solely from charge carriers, we use $\gamma = (\pi^2/3)k_B^2N(E_F)$ to calculate N(EF). We find N(EF) lies between 1.15 × 10²⁴ eV⁻¹ mol⁻¹ and 1.47 × 10²⁴ eV⁻¹ mol⁻¹. These values are in good order of magnitude agreement with band structure calculations, which gave N(EF) ~ 5.1 × 10²² eV⁻¹ mol⁻¹ for La0.67Ca0.33MnO3, especially given the increased doping level in our materials.

Thirdly, we note that the use of a $\beta_3 T^2$ term in the lattice contribution is required to adequately fit the data, even though the upper temperature limit used in the fitting process was only 10 K. Fits from base temperature to 20 K were also performed and also required the inclusion of a $\beta_3 T^3$ term. Fitting over this broader temperature range produces slightly lower values for $\beta_1$. However, the agreement between the fits and the low-temperature portion of the data when fitting over this more extended temperature range was significantly poorer. From $\beta_3$ we calculate the Debye temperature $\theta_D$ using $\theta_D = (12 \pi^2 / 3 p R \beta_3)^{1/3}$, where R is the gas constant and p is the number of atoms in each molecule. For all the samples, $\theta_D$ lies between 333 and 344 K. These values are at the lower end of the range of Debye temperatures observed for the La based manganites for which values between 360–530 K but there is no clear correlation between the value of $\theta_D$ and $\gamma$. In contrast, Woodfield et al. have included a magnetic term $T^{1/2}$ in the fits to their specific heat data for ferromagnetic samples of La1−xSr0.5MnO3. There have been a number of neutron scattering measurements on manganites in which the spin waves have been directly measured so there seems little doubt that spin waves are present in this class of materials. Given a dispersion relation for ferromagnetic spin waves of the form $E = Dq^2 + \Delta$, where D is the spin wave stiffness constant and $\Delta$ is the spin wave energy gap, if $\Delta$ is zero, the magnetic contribution to specific heat per unit volume $C_{mag}$ should be equal to $c_J k_B (k_B T/D)^{3/2}$ where $c_J$ is a constant whose value depends on the lattice type. The absence of a $T^{3/2}$ term may be due to a non zero gap. An inelastic neutron scattering study of Pr0.6Ba0.4MnO3 revealed the existence of a gap of 2.5 ± 0.5 meV. A gap of similar magnitude in these materials would be sufficient to prevent the observation of a spin wave term at low temperatures. Alternatively, the spin waves may be extremely stiff. Values for D of up to 170 meV Å² have been reported. This should give a contribution to C of around 0.2–0.25 J/mol K at 8 K which is ~7–10% of the total signal at this temperature for our FM samples. Although the resolution of the magnetic $T^{3/2}$ contribution is always experimentally difficult, given the presence of the linear electronic term, we feel that a contribution of this magnitude, if present, should be revealed by the fitting procedures adopted here.

For $x < 0.25$, the analysis of the low temperature specific heat data presents a different set of problems. It is clear from Fig. 1 that there is an additional contribution to heat capacity at low temperatures in these samples when compared with the $x = 0.25$ materials. The magnitude of this extra contribution increases monotonically with decreasing Sr content and is most pronounced for the Pr0.6Ca0.4MnO3 end compound. Note that a similar trend is seen in the data for La0.5Sr0.5MnO3 where the undoped end compound is also an antiferromagnetic insulator. Since Pr0.6Ca0.4MnO3 is an insulator at low temperatures it is difficult to justify the inclusion of a linear term in the expression used to fit the data. As a consequence we have attempted to fit the data to

$$C(T) = \frac{\alpha}{T^2} + \beta_3 T^3 + \beta_3 T^5 + \delta T^n. \quad (3)$$

The values of the free parameters obtained by fitting the data up to 10 K can also be found in Table I.

As expected, the values for $\alpha$, the coefficient in the hyperfine term, are similar to those obtained for the Sr rich samples. As regards the lattice contribution to the specific heat, we find that that $\beta_3$ is much smaller than the values obtained for the $x = 0.25$ samples. Reasonably good fits to the data can even be obtained without the inclusion of a $T^3$ term. Whatever fitting strategy is used we see a steady increase in the magnitude of the $\beta_3$ coefficient as the Sr content is reduced. At $x = 0.0$, $\beta_3$ is more than twice the value seen for the $x = 0.25$ compound. This seems unusual as it would suggest that moving from a Sr doping level of $x = 0.25$ to $x = 0.0$ decreases the Debye temperature from 344 to 263 K. It is hard to imagine how such a small change in doping concentration could soften the lattice so dramatically.

This leads us to conclude that the $T^3$ term probably includes an additional antiferromagnetic spin wave contribution. Note that for an antiferromagnetic spin wave spectrum where $E = Dq$, the magnetic contribution to specific heat per unit volume $C_{mag}$ is given by $c_J k_B (k_B T/D)^{3/2}$ where $c_J$ is a constant whose value depends on the lattice type. There is also the significant addition of a $T^2$ term. A previous study of the temperature dependence of the specific heat of pure
LaMnO$_3$, which is also an antiferromagnetic insulator, reported a best fit to the data fit which included a $T^2$ term. In this case a dispersion relation with both ferromagnetic and antiferromagnetic character was invoked to explain the $T^2$ contribution. For Pr$_{0.6}$Ca$_{0.4}$MnO$_3$, we suggest that given the CE magnetic structure, the proximity of this material to a FM ordered state and the evolution of the magnetic order as the temperature increases, it is not surprising that the magnetic contribution to the specific heat data does not follow a simple $T^2$ or $T^3$ temperature dependence.

### B. High-temperature specific heat data

We now discuss the high-temperature specific heat data. In Fig. 2 we show specific heat capacity versus temperature curves for samples with $x=1.0$, 0.75, 0.5, 0.25, and 0.0. At room temperature the heat capacity for all samples is $10^2$–$10^6$ J/mol K, which is $4.2R$. These values agree well with the previous high-temperature specific heat measurements performed on this class of materials and with Dulong and Petit’s law for a system made up of molecules containing five atoms including three “light” oxygen atoms. The Debye temperature of each sample can also be extracted from the high-temperature specific heat data. Unfortunately, the data cannot be fitted using a Debye function over the entire temperature range studied as $\theta_D$ appears to be weakly temperature dependent. However, fits over a more restricted temperature range, or the calculation of $\theta_D$ at a single temperature, give values for $\theta_D$ of between 426 and 433 K. These numbers are consistent with the values calculated from the low-temperature data, given the temperature dependence of $\theta_D$, and are also in line with previously published values of $\theta_D$ for similar materials.

Again we first consider the $x \geq 0.25$ materials which order ferromagnetically. For each sample, we observe a clear anomaly in the specific heat versus temperature curve which marks the onset of long range magnetic order. The temperatures at which these peaks occur agree well with the critical temperatures determined from the magnetization data. Subtracting off a smooth background as a lattice contribution we can see more clearly the contribution to the data due to these transitions. Each transition is marked by a peak in $\Delta C(T)$ around 50 K wide. For the samples with $x \geq 0.5$ these peaks appear to be asymmetric with an additional contribution on the low-temperature side of the transition. The magnitude of the jump seen in the specific heat $\Delta C(T)$ varies from 15–34 mJ/mol K which is 1.8–4.1$R$. This compares with a value of 2.3$R$ expected from a simple molecular field approximation for $S=1.85$ (assuming a 60/40 ratio of Mn$^{3+}$/Mn$^{4+}$) and a $\Delta C$ of 4.8$R$ given by the double exchange model. The magnitude of $\Delta C$ seems to depend on the homogeneity of the sample. If we assume that it is the most homogeneous samples with the largest $\Delta C$ which re-
reflect the true nature of the materials, then the large value of \(\Delta C\) can be explained by reference to the DE model. There is no apparent discontinuity between the lattice heat capacity above and below \(T_C\). Similarly there is no hysteresis seen in the magnetization versus temperature curves on warming and cooling the sample (see the inset of Fig. 4). This indicates the magnetic transitions are second order.

The entropy associated with the transition in each composition, which can be obtained from \(\Delta S_{\text{trans}} = \int (C/T) dT\), lies between 1.4 and 1.5 J/mol K. This is true both for samples in which the transition is sharp, with a large \(\Delta C\), and for samples in which the transition takes place over a more extended temperature range. These entropy values are much smaller than the \(R \ln 4.7 = 12.7\) J/mol K expected from an \(S = 1.85\) spin system. Similar low values have been reported by Ramirez et al.\(^4\). There are several possible ways to account for this “missing” entropy.

The first approach is to assume the transition to a fully ordered ferromagnetic state is only complete well below \(T_C\) and then try to estimate the magnetic contribution to the total heat capacity below the transition temperature using a simple theory such as a mean field model. This requires a knowledge of the exchange constant \(J\). It is possible to estimate \(J\) from the jump in specific heat data at the transition.\(^6,25\) However, in this system we have seen that the magnitude of the jump depends on extrinsic factors such as the homogeneity of the sample. So here we follow Gordon et al.\(^7\) who applied a mean field model to their magnetization data, using \(T_C\) to determine \(J\), and calculate the magnitude of the magnetic contribution to the data. We use 

\[
C_{\text{mag}} = -\frac{3 S R T c e^{2(S + 1)}}{d(M/M_0)^3} dT
\]

where \(M\) is the measured saturation magnetization at a temperature \(T\) and \(M_0\) is the saturation magnetization at \(T = 10\) K. In this way we find, for example, that for the \(x = 0.5\) sample over the temperature interval between 30 and 300 K, the total magnetic contribution to the entropy \(S_{\text{mag}}\) is equal to 12.8 J/mol K (see Fig. 4). Similar values are obtained for the other FM samples. Although the \(C(T)\) curves calculated in this way have the same form as the actual experimental data and give a reasonable value for the total magnetic entropy associated with the transition, the mean field theory clearly over estimates the magnitude of the specific heat close to \(T_C\). This is not totally unexpected, as it is not clear that a simple mean field model with a single exchange constant, is appropriate for this class of materials.

A better solution to the problem of the missing entropy would be to correctly identify the phonon contribution to the specific heat, subtract this term from the data, and then examine the remainder. Unfortunately, there are no “nonmagnetic” analogs of \(\text{Pr}_{0.6} (\text{Ca}_{1-x}\text{Sr}_x)_0.4\text{MnO}_3\). One potential solution is to choose a ferromagnetic sample of \(\text{Pr}_{0.6} (\text{Ca}_{1-x}\text{Sr}_x)_0.4\text{MnO}_3\) for which \(T_C\) is lowest (in this case \(x = 0.25\)) and use the data at temperatures well above \(T_C\) as being representative of the nonmagnetic contribution. Similarly we could choose a sample for which \(T_C\) is high and use the data at temperatures well below \(T_C\) to estimate the nonmagnetic phonon contribution at lower temperatures. In this way, we can estimate a non magnetic background for the entire temperature range of interest. This approach presupposes that there are no short range magnetic correlations above \(T_C\) and that well below \(T_C\) there is no magnetic contribution to the data. For the \(x=0.25\) compounds, if we exclude the regions around the \(T_C\) of each sample, we find that all the specific heat versus temperature curves coincide. Deviations for \(x = 1.0\) at 100 K are due to a structural phase transition. This suggests that either there is no contribution to \(C(T)\) with a magnetic origin at temperatures well away from the transition temperature of each individual material, or that the magnitude of this magnetic contribution is more or less constant, irrespective of the value of \(T_C\). It is certainly possible for a system in which there are two or more exchange constants, that the magnetic contribution to the specific heat can be made to be nearly independent of the value of the transition temperature at temperatures well away from \(T_C\). Alternatively, it may be that there really is very little magnetic contribution to the specific heat within the temperature range studied. One possible explanation for this is that a considerable amount of entropy is given up at temperatures much higher than \(T_C\), due to the presence of short range correlations. There is experimental evidence that magnetic excitations persist at temperatures well above \(T_C\) in this class of materials.\(^26\) We have also noted clear deviations from Curie-Weiss behavior in our magnetic susceptibility data in the paramagnetic state of these materials. These short range correlations may take the form of magnetic clusters of Mn ions or may be related to the presence of Jahn-Teller polarons which form at much higher temperatures. We also note that for \(x \geq 0.25\), the \(\text{Pr}_{0.6} (\text{Ca}_{1-x}\text{Sr}_x)_0.4\text{MnO}_3\) materials have an insulator-metal transition at \(T_C\). We may therefore expect a reduction in the change in entropy associated with this transition, due to a localization of the charge carriers as the systems is warmed through \(T_C\). However, an estimate of \(\Delta S_{\text{trans}} = \int (\gamma T/T) dT\) using \(\gamma\) values extracted from the low temperature data shows that this mechanism can account for no more than 1.7 J/mol K of the missing entropy.

Finally, we discuss the high-temperature specific heat data of the charge ordered, AFM \(x = 0.0\) sample. In this case there are two clear anomalies in the data. There is broad peak
centered around 160 K. This marks the onset of antiferromagnetic order. There is a much larger peak at 230 K which corresponds to the charge ordering transition in the system. Once again, both these features can be made more apparent if we subtract off a smooth background from the data (see Fig. 3). At the charge ordering transition, which involves a localization of mobile charge carriers with the formation of a well defined Mn$^{4+}$/Mn$^{3+}$ sublattice, there is also a lowering of the crystallographic symmetry from an orthorhombic $Pnma$ to a monoclinic $P21/m$ structure. This structural phase transition is accompanied by rapid changes in the lattice parameters and bond lengths. As a result, it is not unexpected that this feature is particularly distinct in the specific heat versus temperature data. The entropy associated with this transition amounts to nearly 2 J/mol K. In contrast a lower bound on the entropy developed at the AFM transition is only 0.6 J/mol K. This small value again suggests that either a sizable fraction of the spin entropy is given up at lower temperatures, as the system evolves from a canted CE structure with two magnetically ordered Mn sublattices, through a collinear structure at 150 K and finally into a paramagnetic state at 160 K, or that short range magnetic correlations persist to temperatures well above $T_N$. In conclusion, we have measured the specific heat of a number of Pr$_{0.6}$Ca$_{1-x}$Sr$_x$0.4MnO$_3$ ($0 \leq x \leq 1$) manganite samples. Our measurements indicate that for $x \geq 0.25$, the samples are well behaved metallic ferromagnets with small $\gamma$ values. Previously observed enhancements in $\gamma$ are probably due to a low-temperature hyperfine contribution to the data. However, no $T^{1/2}$ spin wave term can be resolved in the $C(T)$ data. In contrast, the low-temperature specific heat data of the $x \leq 0.25$ AFM, charge ordered materials contain an additional contribution which can be attributed to magnetic order. In the high-temperature data, there is clear evidence for the magnetic, structural and charge ordering transitions which occur at various different temperatures and doping levels in these materials.

**ACKNOWLEDGMENTS**

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25. For each sample, a nonmagnetic contribution was estimated by fitting a fourth order polynomial to the $C$ versus $T$ curve at temperatures well away from any anomalies in the data. As such, this background is only a rough approximation of the real lattice contribution to the specific heat.
27. In a neutron scattering study of La$_{1-x}$Ca$_x$MnO$_3$ with $x=1/3$, it has been shown (Ref. 22) that the spin wave stiffness at $T_C$, $D(T_C)$ is equal to $1/2D(T=0)$. 
28. At least 1.2 J/mol K of entropy is developed around the magnetic transition of charge ordered La$_{0.35}$Ca$_{0.65}$MnO$_3$ (Ref. 4).