Specific heat of single-crystalline $Pr_{0.63}Ca_{0.37}MnO_3$ in the presence of a magnetic field

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We present the results of a study of the specific heat on a single crystal of $Pr_{0.63}Ca_{0.37}MnO_3$ performed over a temperature range 3–300 K in the presence of 0 and 8 T magnetic fields. An estimate of the entropy and latent heat in a magnetic field at the first-order charge-ordering (CO) transition is presented. The total entropy change at the CO transition, which is ≈ 1.8 J/mol K at 0 T, decreases to ~ 1.5 J/mol K in the presence of a 8 T magnetic field. Our measurements enable us to estimate the latent heat $L_{CO} \approx 235$ J/mol involved in the CO transition. Since the entropy of the ferromagnetic metallic (FMM) state is comparable to that of the charge-ordered insulating state, a subtle change in entropy stabilizes either of these two states. Our low-temperature specific heat measurements reveal that the linear term is absent at 0 T and surprisingly not seen even in the metallic FMM state.

I. INTRODUCTION

The discovery of a number of fascinating properties like colossal magnetoresistance (CMR), charge and orbital ordering, and electronic phase separation in manganites with generalized formula $R_{1-x}A_xMnO_3$ (R being a trivalent rare-earth ion, A a divalent alkaline-earth element) has resulted in a spurt of research activities.[1,2]

For certain values of x, close to 0.5, these manganites undergo a first-order transition at a certain temperature T_{CO} to a charge-ordered insulating (COI) state where the Mn^{3+} and Mn^{4+} species arrange themselves in a commensurate order in the lattice.

The charge ordering transition in these oxides is accompanied by a large change in volume and hysteresis in resistivity and is believed to be a first-order transition. A fascinating aspect of the COI state (which is also accompanied by orbital ordering) is that it is unstable under an applied magnetic field and there is an insulator-metal transition (melting) of the COI state to a ferromagnetic metal state (FMM) below a temperature T_{MH}.

In this paper we have investigated the specific heat and related thermodynamic quantities in a single-crystalline CO system over a wide temperature range (3 K$<T<$300 K) and in a magnetic field upto 8 T which can melt the CO order. A study of the specific heat over an extensive temperature range is crucial in understanding the nature of the CO transition and in addition it can provide values of various fundamental parameters of manganites like the density of states at the Fermi level $N(E_F)$, the Debye temperature θ_D, ferromagnetic-antiferromagnetic (AFM), spin-wave stiffness constant, etc.

Measurements of the specific heat in manganites particularly with CMR composition has been reported before, par-ticularly in the low-temperature region. In the CO systems there are reports of specific heat measurements in both single and polycrystalline samples mainly at low temperatures. Specific heat measurements in CO systems near T_{CO} have been done in polycrystalline samples and no magnetic field data have been reported. There exist no data on the thermodynamics associated with the transition at T_{MH}.

The charge ordering transition in these oxides is believed to be a first-order transition, as mentioned before. Measurements across the CO transition should therefore show a discontinuous jump in entropy as the compound absorbs latent heat from the bath to transform to a new phase. However, to date there exists no proof from calorimetry that the transitions are indeed first order and whether a latent heat is released at the transition. There has been no calorimetric investigation of the melting of the COI state to a FMM state, the transition which is also believed to be a first-order transition.

In this paper we investigate these fundamental issues related to changes in entropy and latent heat across the charge-ordering transition near T_{CO} and T_{MH} in a single crystal of $Pr_{0.63}Ca_{0.37}MnO_3$. $Pr_{1-x}Ca_xMnO_3$ happens to be a prototypical and perhaps the most studied charge-ordered system. Due to its low tolerance factor, it remains insulating for all values of x. For $x=0.37$ composition, charge and orbital ordering occurs at T_{CO} (≈ 235 K), while a long-range AFM order sets in only below T_N (≈ 170 K). A small ferromagnetic component appears with the canting of AFM spins at a lower temperature T_{CA} (≈ 30 K). Though there have been a number of studies of the low-temperature specific heat of this particular system ($T<20$ K), a clear picture is yet to be emerge on the presence (or absence) of a linear term in specific heat. Recently there have been reports of a large linear contribution to the specific heat and the appearance of excess

specific heat associated with charge ordering[3] in this system. Since such a linear term is often associated with a electronic contribution to the specific heat, the appearance of this term in an insulating sample is intriguing.

In this paper, we have also investigated the low-temperature region and reached certain definite conclusions about the linear term.

In our experiments we have specifically asked the following questions.

(i) Is it possible to identify the relevant transitions in zero and finite magnetic fields through calorimetric measurements?

(ii) What latent heat is released and the entropy change across the first-order transitions, one at T_{CO} in zero magnetic field and the other at T_{MH} in 8 T magnetic field?

(iii) When the FMM state is obtained from the COI state in the presence of a magnetic field, do we obtain a linear term (arising from electronic contribution) in the specific heat?

(iv) Do we see a linear term in the specific heat in the COI state as reported by some investigators?

The remainder of the paper is divided into two principal sections. In Sec. III, we present and discuss the experimental data in the region $T \geqslant 50$ K which essentially encompasses the region where most of the transition occurs and this also happens to be the region where no experimental data have been reported in the past either in the presence of a magnetic field or in a single crystal. The second major section (Sec. IV) refers to the data at low temperatures where issues like the linear term in the heat capacity, the Debye term, spin-wave contributions, etc., are looked into. In this region there are past studies, as mentioned earlier, and we compare our results on these material with results from other CO systems.

II. EXPERIMENT

The crystal used in our experiment has been grown by the floating zone technique and has been used in a number of previous experiments by our group.[4,5]

The resistivity (ρ) vs T curve in zero field and the curve in a field of $H = 8$ T are shown in Fig. 1. The COI state can be melted into a FMM state by the application of a magnetic field of 8 T at $T_{MH} \approx 90$ K. In the presence of a magnetic field the region $T_{MH} < T < T_{CO}$ is termed a "mixed charge order" (MCO) region, where the COI phase coexists with the FMM phase. We have used a semiadiabatic heat pulse technique to measure the specific heat in a wide temperature range of 2–300 K and in 0 and 8 T magnetic fields.

III. SPECIFIC HEAT AT HIGH ($T \geqslant 50$ K)

In Fig. 2 we show the specific heat (C_p) data over an extended temperature range 3–300 K for both 0 and 8 T. The most prominent feature is the sharp peak at T_{CO} both for $H = 0$ and 8 T. The peak is much larger and sharper compared to that seen in polycrystalline materials[6] (which is also plotted in the same graph). The peak at T_{CO} retains its narrowness and sharpness at $H = 8$ T while it shifts to lower T with $dT_{CO}/dT \approx -1$ K/T. In Fig. 3 we show the region
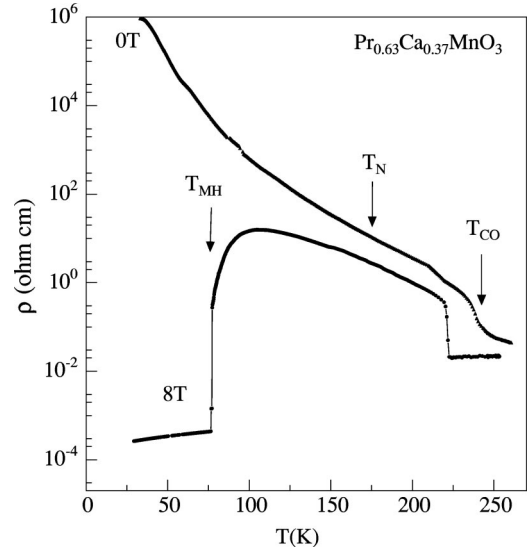

FIG. 1. The temperature dependence of resistivity of $Pr_{0.63}Ca_{0.37}MnO_3$ in presence of 0 and 8 T magnetic fields.

close to T_N. The graph shows the actual observed steplike feature in C_p (at $H = 0$ T) at T_N. In the same graph we show C_{exc} after subtraction of the lattice contribution (the procedure for subtraction of the lattice contribution is given in the next subsection). A peak in $C_{exc} \approx 6$ J/mol K at T_N is visible. This feature is suppressed by the application of a magnetic field of 8 T. The entropy change $\Delta S_{exc}(T_N)$ associated with this transition has been estimated to be $\approx 0.5 - 0.8$ J/mol K.

Lee *et al.*[6] reported for $Pr_{0.6}Ca_{0.4}MnO_3$ (polycrystal) $\Delta S_{exc}(T_N) \approx 0.6$ J/mol K at $T_N = 160$ K. Ramirez *et al.*[7] for $La_{0.35}Ca_{0.65}MnO_3$ (polycrystal) obtained $\Delta S_{exc}(T_N) \approx 1$ J/mol K. It can be seen that all these are much less than that what one would expect from a complete spin ordering.
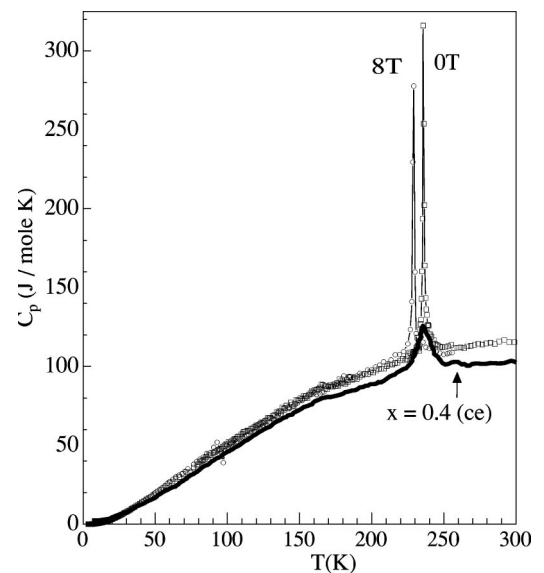

FIG. 2. C_p of single-crystalline $Pr_{1-x}Ca_xMnO_3$ ($x = 0.37$) over 3–300 K in the presence of 0 and 8 T magnetic fields. Also plotted is the C_p of the polycrystalline $x = 0.4$ composition.
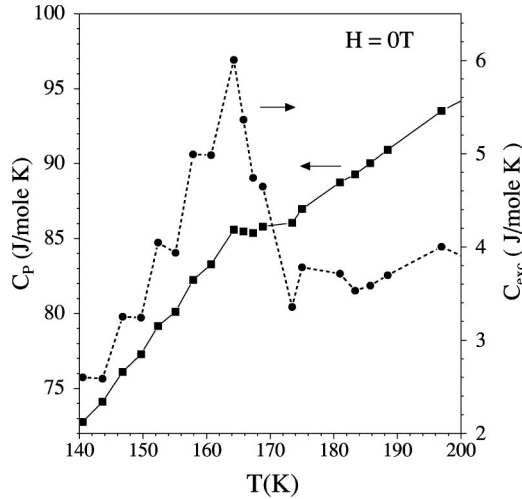
FIG. 3. C_p and C_{exc} close to T_N in $H=0$ T.

The calorimetry data therefore points towards an incomplete spin ordering at T_N.

Another very interesting feature in our calorimetry data is a clear signature of the magnetic-field-induced transition at $T_{MH} \approx 78$ K (see Figs. 2 and 9). This small yet distinct feature, discussed in detail later on, is the first signature of field-induced melting in a calorimetry experiment.

A. Estimation of the lattice contribution

In this subsection we describe the procedure to estimate the lattice contribution to the specific heat, the background on which the specific heat contributions by the other degrees of freedom add up. Proper estimation of the lattice contribution will thus allow us to get the contribution of CO and magnetic ordering to C_p. We define C_{exc} as

$$C_{exc} = C_p - C_{lattice}. \tag{1}$$

According to the Dulong- Petit law, the limiting heat capacity at high temperature for a compound with r atoms per molecule is expected to be $3rR$, where R is the gas constant.[8] In our case ($r=5$) this limiting value of the lattice (vibrational) heat capacity turns out to be ≈ 125 J/mol K. From our data we find that at $T=300$ K, the observed C_p is $\approx 90\%$ of the Dulong-Petit value. For most published data on manganites, C_p at room temperature reaches this value ~ 100–120 J/ mol K. This signifies that the bulk of the contribution indeed comes from the vibrational heat capacity in this temperature range. This contribution must be subtracted from the observed data to obtain the excess specific heat. We have obtained the lattice contribution $C_{lattice}$ by fitting C_p in a region 40 K$\leq T \leq$150 K using three standard models as described below. The calculated $C_{lattice}$ is then extrapolated to $T>150$ K. Since we are interested in C_p in the range 80–300 K, the lower temperature for the lattice contribution has been limited only to 40 K. The upper limit of 150 K was considered since it was lower than the AFM and CO transition temperatures. We have not estimated the background by including the data about T_{CO}. We are of the opinion that there is structural transition and modification associated with the CO transition. As a result it is not advisable to include data above T_{CO} in the estimation of the lattice heat capacity below T_{CO}. The following models were used for estimating the background lattice contribution.

1. Einstein model

From Ref. 8, $C_{Einstein} = 3rR\Sigma_i a_i [x_i^2 e^{x_i}/(e^{x_i}-1)^2]$, where $x_i = h\nu_E/K_B T_i$. In this model, all the $3rN$ independent oscillators populate three optical modes in ratios $a_1:a_2:a_3$ having Einstein frequencies $h\nu_{E_i}$. The best fit to the data is given the three Einstein modes with $h\nu/K_B = 145$ K, 410 K, and 625 K. It is interesting to note that a recent Raman measurement on $x=0.37$ composition observed optical modes at ≈ 360 K, 417 K, and 648 K. The 417 K and 648 K modes nicely match with those seen in our specific heat measurements.[9]

2. Debye model

From Ref. 8, $C_{Debye} = 9rR/x_D^3 \int_0^{x_D} x_D^4 e^{x_D}/(e^{x_D}-1)^2 dx_D$, where $x_D = h\nu_D/K_B T$. The specific heat is due to collective low-frequency oscillations of phonons with a cutoff frequency given by $h\nu_D/K_B$. For our sample, the best fit was obtained with $\theta_D = 470$ K. This is typically the value of θ_D seen in most oxides.

3. Thirring model

From Ref. 10, $C_{Thirring} = 3rR\Sigma_{n=0}^{\infty} B_n u^{-n}$, where $u = [(T/T_b)^2 + 1]$ The harmonic portion of the lattice specific heat can be expressed in a series with the above form where $T_b \approx \theta_D/2\pi$.[11]

The above expansion permits the harmonic portion of the lattice specific heat to be fitted reasonably well down to temperatures ~ 50 K even when the Debye temperature is ~ 500 K. In our case, $T_b = 65$ K and we used n up to 50. The T_b gives an estimated $\theta_D \approx 410$ K, which is close to that obtained from fitting the data with Debye model.

In Fig. 4 we have shown the deviation of the observed data from the fit [i.e., $\Delta C/C = (C_{obs} - C_{calc})/C_{obs}$] in order to ascertain the extent of uncertainties involved in the background subtraction. We find that for $T<100$ K the Debye model shows a large systematic deviation. The Thirring model shows a systematic deviation above 150 K (not shown in the graph). We find that over the whole range the least uncertainty is shown by the Einstein model (maximum deviation from fit $\pm 5\%$) and this is a random deviation.

We have used the same $C_{Lattice}$ for both $H=0$ and $H=8$ T. We found that if we fit the C_p at $H=8$ T from 50 to 140 K to the above models as we have done for the C_p at $H=0$ T case, we end up in getting essentially the same $C_{Lattice}$ using the Einstein model. There is a small ($<10\%$) systematic deviation (for the Einstein model) which is not numerically significant to affect our results. This is shown in the inset of Fig. 4. For compounds containing Pr^{3+}, C_P may contain a contribution coming from the crystal field. We have estimated this crystal field contribution or C_{xtal}, the crystal field data available for iso structural compounds $PrNiO_3$ and $PrGaO_3$. We find that in the range of
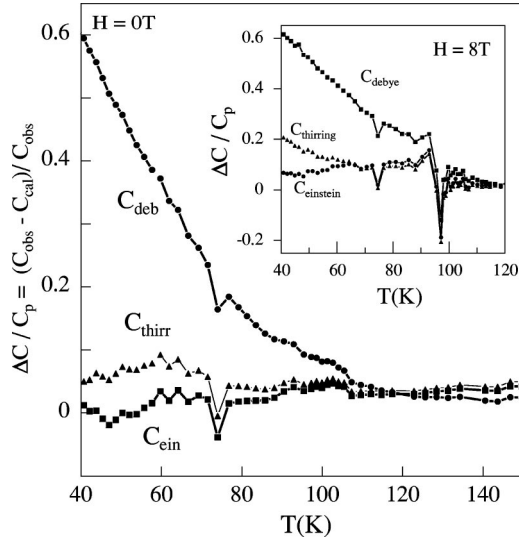
FIG. 4. Deviation of C_p from the fit for different models. The inset shows the same near T_{MH} in $H=8$ T.

interest (100 K$<T<$300 K) this crystal field contribution $<$7% at 100 K and is $<$2% at 300 K.[12]

B. C_{exc}

In Fig. 5 we have plotted the value of C_{exc} for both $H=0$ and $H=8$ T for $T>120$ K. The data show C_{exc} using all the three models. The C_{exc} data in the region close to T_{CO} are truncated in Fig. 5, because in this region C_{exc} is very large. In this temperature range the differences in C_{exc} obtained after subtraction of the lattice contribution is well within 1–2 J/mol K for the Debye and Einstein models. The Thirring model shows a systematic deviation for $T>150$ K. Considering all the models we find that near T_N the uncertainty is the largest since C_{exc} is low and this can be as large as $\pm25\%$. *However, close to the CO transition when C_{exc} shoots up to ≈220 J/mol K. The uncertainty in the background estimation falls below $\pm2\%$.*
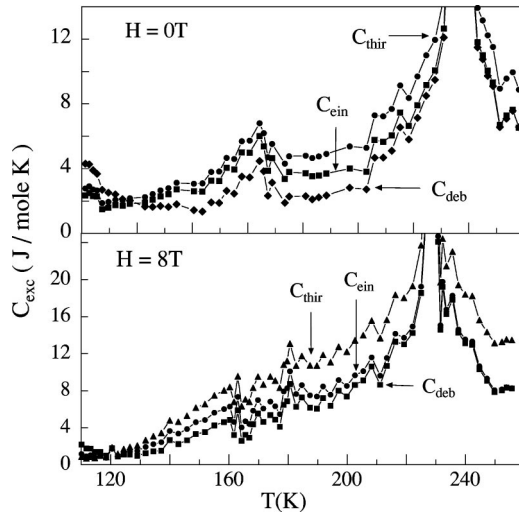

FIG. 5. C_{exc} obtained after subtracting the lattice background (as determined by the three models) for both $H=0$ and 8 T.

The C_{exc} data also show clearly that barring the small region around T_N (where $C_{exc}\approx10\%$ of C_p) and near T_{CO} (where $C_{exc}>50\%$ of C_p) the contribution by other degrees of freedom compared to the lattice contribution is negligible in the temperature range $T>50$ K.

C. Entropy change near T_{CO} in $H=0$ and $H=8$ T

A phase transition is signaled by a singularity in a thermodynamic potential such as the free energy. If there is a finite discontinuity in one or more of the first derivatives of the free energy, the transition is first order. At a first-order transition one expects a discontinuous jump in the entropy. At the charge ordering transition (which is conjectured as a first-order transition based on the observed hysteresis in transport data on field and temperature cycling), our system is expected to absorb the latent heat of transformation to transform from a charge-ordered phase to a charge-disordered phase as it is heated through T_{CO}. The temperature should remain untill this process is complete and the entropy change is given as

$$\Delta S_{21}=S_2-S_1=L_{21}/T, \qquad (2)$$

where S_1 and S_2 are the entropies of phases 1 and 2, and L_{21} is the latent heat associated with the phase transformation. At a first-order transition, since the entropy changes discontinuously, the specific heat is actually undefined. Because at the transition point the temperature does not change when heat is applied, one would expect a δ-function like behavior. In reality, however, one rarely sees such a δ-function-like behavior of C_p because the transition can get broadened either by the process of measurement or by the quality of the sample. This makes a part of the expected entropy change become continuous and it shows up as a finite measurable specific heat. Interestingly, it has only been very recently that the expected features in specific heat in a first-order transition have been seen experimentally in rare-earth compounds.[13] In the following discussion, we have to keep in mind the above special features since we are measuring the specific heat near a transition which is expected to be first order. In Fig. 6, C_{exc}/T is plotted as a function of T within a small interval of $\pm$ 25K around T_{CO} for both $H=0$ and 8 T. In Fig. 7, we have shown the excess entropy $S_{exc}(T)$ associated with this transition. The entropy $S_{exc}(T)$ for $T>200$ K is calculated by numerically integrating C_{exc}/T as $S_{exc}(T)=\int_{200}^{T}C_{exc}/T\,dT$. The lower limit of the integral is purely a matter of convenience. It is far removed from T_N and T_{CO} and at $T=200$ K, $C_{exc}\approx3\%$ of C_p and is negligible. We estimate the total change in entropy, ΔS_T, by using linear extrapolation of the entropy values from above and below to T_{CO} as depicted in the Fig. 7. $\Delta S_T\approx1.8$ J/mol K at 0 T and it decreases to 1.5 J/mol K at 8 T. This total change in entropy takes place over an interval of ≈10–15 K around T_{CO}. The magnitude of $\Delta S_T(0$ T) agrees well with that found in polycrystalline samples by Lees *et al.*[6] by integrating the area under the peak in C_{exc}/T. In polycrystalline $La_{0.35}Ca_{0.65}MnO_3$ Ramirez *et al.*[7] obtained $\Delta S_T\approx5$ J/mol K. In polycrystalline $Y_{0.5}Ca_{0.5}MnO_3$ our group observed $\Delta S_T\approx2.5$ J/mol K.[14] The total entropy change at

FIG. 6. C_{exc}/T around T_{CO} in $H=0$ and 8 T.

FIG. 8. Varying sharpness and width of C_p near T_{CO} for two different temperatures rise $\Delta T = 0.5$ and 1 K.

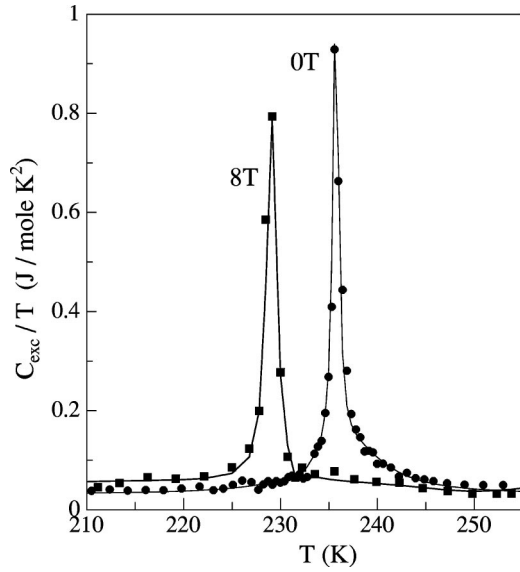FIG. 7. Excess entropy S_{exc} as calculated from numerically integrating C_{exc}/T around T_{CO} in $H=0$ and 8 T.

the CO transition thus seems to be a fraction of what one would expect from an order-disorder transition. The error in the estimation of the entropy change arising from the uncertainty in estimation of background $C_{Lattice}$ is not more than 5%. In a narrow temperature range over which the transition occurs the change in entropy being the difference of two quantities with similar background, the error arising from the estimation of the background is not severe.

The charge-ordered phase is expected to have a lower entropy than the charge-disordered insulating phase at $T > T_{CO}$. This implies that the sample absorbs latent heat to transform from the charge-ordered phase to the disordered phase. We would expect that at least a part of the entropy change ΔS_T released as latent heat is absorbed from the total heat ΔQ supplied during the heat-pulse experiment and the
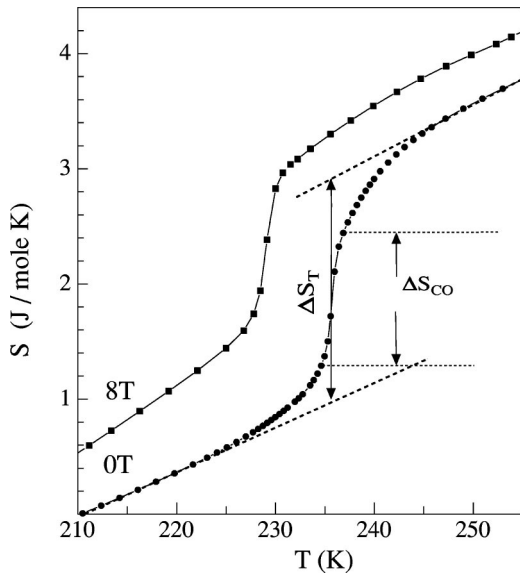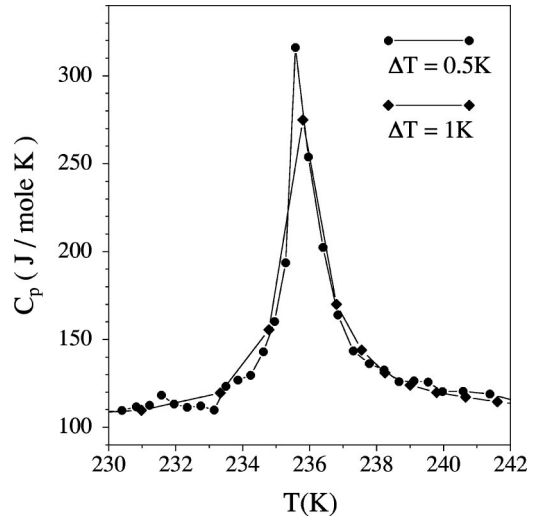
sample temperature remains quite constant throughout the process. Since the change in sample temperature (ΔT) is quite small, the specific heat $C_p = (dQ/dT)_p$ shows a very sharp peak near T_{CO}. As discussed before at a first-order transition $\Delta T \rightarrow 0$ and ideally C_p should be a δ function at the transition temperature.

The peak, however, is broadened due to two reasons.

(a) Crystal quality. In most cases the expected δ function gets broadened by sample quality. The real crystal contains some defects and inhomogeneities which would lead to a broadening of the peak. With improved quality of the sample, the peak would be larger and sharper. For oxides containing multiple chemical constituents it is quite likely that such is the case. As shown in Fig. 1, where we have compared the C_p of a ceramic pellet and a single crystal, the single crystal has a much higher and narrower C_p at T_{CO} as compared to the ceramic sample.

(b) Measurement broadening. The second reason for broadening of the peak is connected to the measurement procedure itself. C_p measurement involves measuring a finite-temperature jump ΔT following the heat pulse ΔQ. Since C_p is well behaved in the region away from T_{CO}, it does not depend much on the size of the temperature rise ΔT (as long as C_p is not a very steep function of T). However, close to T_{CO}, the height as well as the width δT of C_p sensitively depends on ΔT.

We have measured the latent heat by measuring C_p with different ΔT as suggested by Gschneidner *et al.*[13] A sample of the data is shown in Fig. 8. We find that while away from T_{CO} there is no dependence of C_p on the rise of ΔT, as expected, the peak becomes narrower and higher when the size of ΔT decreases as we approach T_{CO}. This continues untill $\Delta T \leqslant 0.5$ K. For this value we reach a limiting width (at half maxima) $\delta T \approx 2$ K. We believe that for $\Delta T \leqslant 0.5$ K, the width of the peak is not determined by the measurement but by the crystal quality. This observation sets a limit to the height and width of C_p. We find from our measurement that the latent heat $L_{CO}/T_{CO} = \Delta S_{CO}$
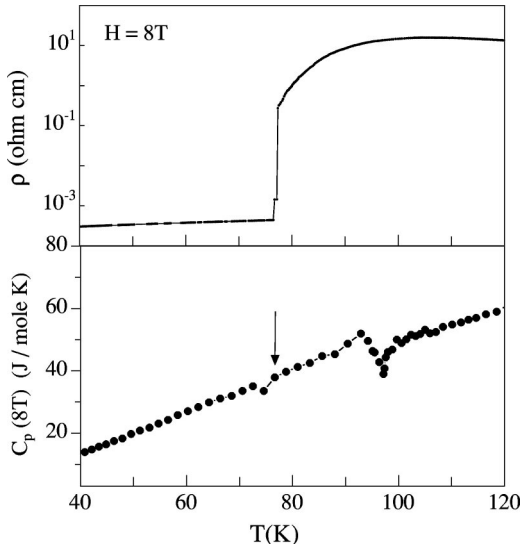
FIG. 9. C_p and resistivity near the T_{MH}. The arrow marks the melting of the COI state.

FIG. 10. A comparison of C_p of $Pr_{1-x}Ca_xMnO_3$ in the low-temperature regime as observed by different groups, $x = 0.5$ (sc), 0.45 (ce), 0.35 (ce) (Ref. 3), $x = 0.4$ (ce) (Ref 6) and $x = 0.37$ (sc) is our sample.

~1 J/mol K. A similar value of ΔS_{CO} was obtained for $H = 8$ T. Our estimate of the latent heat is a lower bound of the true latent heat and with a better crystal preferably with a transition width < 1 K, $\Delta S_{CO}/\Delta S_T$ will increase substantially and may even $\rightarrow 1$, as expected for a strong first-order transition. We note that such a narrow peak might arise from a very narrow second-order transition that has been broadened by defects or inhomogeneities. However, we find that the applied field shifts the position of the peak but does not appreciably broaden the peak. This we take as proof of a first-order transition at T_{CO}.

D. Entropy change near T_{MH} in 8 T

In a field of 8 T the low-temperature phase is an FMM or a spin-aligned metal, allowing for spin canting. But the phase is metallic as can be seen from Fig. 1. On heating, the FMM state (8 T) becomes unstable towards COI state formation and makes a transition to the MCO state at T_{MH}. This is accompanied by a jump in ρ. We would like to ask if there is a change in entropy associated with the melting of the COI state to FMM state at T_{MH}, This question is interesting because both phases have ordering of a kind; in addition, the FMM phase is expected to the have extra entropy due to presence of free electrons. A close look at the region $T \approx 95$ K, as shown in Fig. 9, shows a small dip in C_p which as explained below can be considered as a signature of this melting. It is important to note that, as expected in zero field, this feature is absent. As shown in Fig. 9, $C_p(8$ T) starts to show change at $T = T_{MH} \approx 88$ K where ρ shows a jump on heating and the specific heat transition is complete at 100 K after a small dip in C_p, where the resistivity transition also stops.

The small dip in C_p is associated with a small heat release of ≈ 10 J/mole at around 95–100 K on heating. This suggests that on heating the FMM phase, stable in 8 T for low T, starts to disorder. This probably destabilizes the FMM phase with regions of high-resistivity COI regions appearing in it.
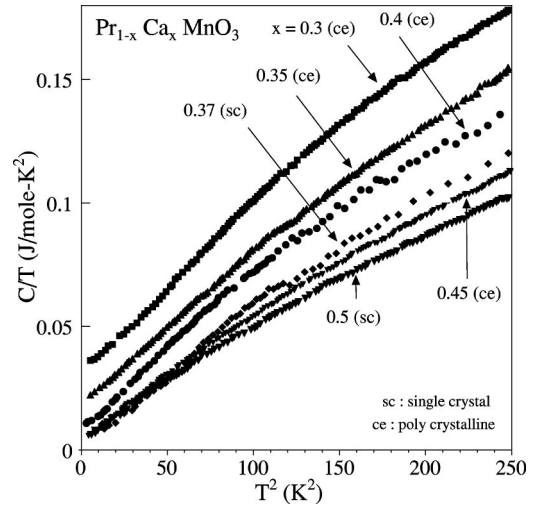
Eventually at $T \approx T_{MH}$ the insulating regions increase in size and ρ shows a jump in ρ. The resistivity transition has an element of percolation associated with it and thus occurs at a different volume fraction of the new phase in contrast to the specific heat transition which occurs mainly when the bulk of the sample is transformed. Nevertheless, the small but distinct change in C_p close to T_{MH} is clearly seen.

In the temperature range $T_{MH} < T < T_{CO}$ in a magnetic field(i.e., the MCO region) we find an interesting effect. The thermal relaxation time of the sample increases by more than one order of magnitude. This anomalously large relaxation is not observed at any temperature range in zero field or for $T > T_{CO}$ and $T < T_{MH}$ in H=8 T. The existence of this large thermal relaxation necessitated that the sample be properly equilibrated before the data are taken. We have done that and the data presented here are taken after the sample has been properly equilibrated thermally. The thermal relaxation, however, is interesting in its own right and has been discussed in a separate publication.[15]

IV. LOW-TEMPERATURE C_p IN 0 AND 8 T MAGNETIC FIELD

As has been pointed out before, the issue of low-temperature specific heat ($T < 10$ K) is controversial in manganites showing charge ordering, particularly in the $Pr_{1-x}Ca_xMnO_3$ system. A large number of observations on the low-temperature specific heat are available for different compositions of $Pr_{1-x}Ca_xMnO_3$, mostly in polycrystalline pellets and some in single crystals.

In Fig. 10 we show the specific heat data of our sample with that of different compositions as obtained by different groups.[3,6] Such a comparison is meaningful because it brings out the essential similarity and differences in these materials. A large linear term [$\gamma \approx 30.6$ mJ/mol K^2 for $x = 0.3$ and $\gamma \approx 15.7$ mJ/mol K^2 for $x = 0.35$ (Ref. 3)] appears in polycrystalline samples with $x = 0.3$ and $x = 0.35$ composition
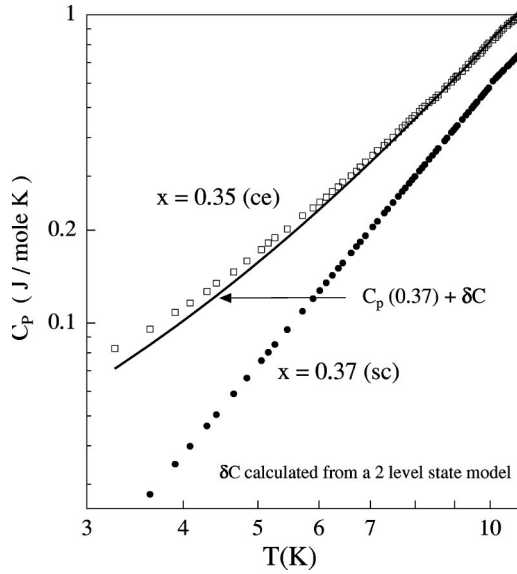
FIG. 11. The excess specific heat δC as seen in the polycrystalline sample arising due to presence of two-level states.

FIG. 12. The low-temperature C_p of single-crystalline $Pr_{0.63}Ca_{0.37}MnO_3$ in $H=0$ and 8 T. The solid line is the fitted equation.

which decreases as $x \rightarrow 0.5$. We note that such a large linear γ has not been seen any of the single-crystal data. From a comparison of the data shown in Fig. 10 we can reach the following conclusions.

(i) The polycrystalline ceramic samples have higher specific heat than the single-crystal samples.

(ii) There is a clear trend that the specific heat of the ceramic samples decreases as we approach $x=0.5$. In particular, the linear term in the specific heat is only observed for the ceramic samples and it decreases with increasing x.

(iii) The specific heat of the single-crystal samples with compositions $x=0.37$ and 0.5 are very similar for $T < 10$ K.

In Fig. 11 we have compared the specific heat of two close compositions: a polycrystalline $x=0.35$ sample[3] and a single-crystal sample with $x=0.37$ composition. The comparison is to elucidate how much of the excess specific heat is due to polycrystallinity and can we infer a likely origin of the excess specific heat. There are two mechanisms that can contribute to the excess specific heat: (1) Due to grains of small dimensions,[16] and (2) due to two-level-systems (TLS) arising due to disorder as in amorphous solids and several disordered crystals.[16] If the excess specific heat is due to grains, then δC can be expressed as $\delta C = C_1 T + C_2 T^2$, where the coefficients C_1 and C_2 are related to the average grain diameter $\langle R \rangle$ as $\langle R \rangle = k_B [6 \hbar v_{sound} C_1]^{-0.5}$, where v_{sound} is the sound velocity in the crystal.[16] We can fit the experimentally observed C_{poly} to the equation $C_{poly} = C_{sc} + \delta C$. Using C_{sc} from our observed data and the above statement of δC we obtain an estimate of the average grain size $\langle R \rangle$ and we obtain $\langle R \rangle \approx 10^{-4}$ μm which is far too small compared to the typical $\langle R \rangle > 1$ μm seen in most polycrystalline samples. We can thus rule out a finite grain size as the source of the excess specific heat. If the excess specific heat δC arises from TLS's then it can be fit to a form $\delta C = C_1 T + C_2 T^3$. This would arise from TLS's with a density
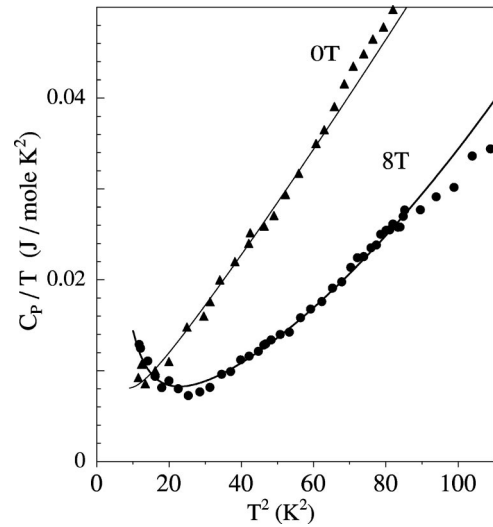
of states $P(E) = \tilde{a} + \tilde{b} E^2$, where $\tilde{a}$ and $\tilde{b}$ are constants.[16] Using this statement for δC we then fitted the observed C_{poly} as had been done before. The fit is shown in Fig. 11. From the fitted parameters C_1 and C_2, we arrive at values of $\tilde{a} \approx 2.3 \times 10^{35}$ erg^{-1}/cm^3 and $\tilde{b} \approx 1.5 \times 10^{35}$ erg^{-3}/cm^3. These values are quite comparable to but somewhat larger than those obtained in glasses. We conclude that the extra specific heat of the polycrystalline samples arises from excitations which behave as TLS's. We have no clear understanding of the origin of these TLS's but we can speculate that they will arise from incomplete orbital and charge order that can happen in polycrystalline samples due to random strains. What is needed for TLS's to occur is to have a multitude of ground states with almost degenerate energy. This can actually be due to the predominant incommensurate charge ordering as seen in both $x=0.35$ and $x=0.37$ compositions. As the charge ordering becomes commensurate with the lattice with $x \rightarrow 0.5$, the difference in the specific heat between the polycrystalline and the single-crystal samples decreases. We thus suggest that the disorder in polycrystalline samples gives rise to TLS low-energy excitations typically with energy ≤ 10 K, and as $x \rightarrow 0.5$, $P(E) \rightarrow 0$.

Next we attend to the low-temperature data taken on our single-crystal sample. Figure 12 shows the specific heat data for the $x=0.37$ sample plotted as C_p/T vs T^2, a customary way to plot the data in anticipation of a linear term. It is clear that the linear term is absent in the COI state. This is not surprising for an insulating sample the linear term was also absent in the specific heat data observed in the ceramic samples of $x=0.4$ by Lees et al.[6] Neglecting the linear term, we have fitted the our observations to the following relation:

$$C_p = \alpha T^{-2} + \beta_3 T^3 + \beta_5 T^5, \qquad (3)$$

where αT^{-2} is the hyperfine contribution caused by the local magnetic field at the Mn nucleus due to electrons in unfilled shells, and $\beta_3 T^3$ and $\beta_5 T^5$ are the lattice contribution to the

TABLE I. The fitting results for the C_p of $Pr_{1-x}Ca_xMnO_3$ as obtained by various groups. The units of different quantities are $\alpha(mJ\,K/mole)$, $\gamma(mJ/mol\,K^2)$, β_3 $(mJ/mol\,K^4)$ and β_5 $(\times 10^{-4}\,mJ/mol\,K^6)$.

x $(Pr_{1-x}Ca_xMnO_3)$	α	γ	β_3	β_5
0.3 [a]	63.0	30.6	0.30	
0.35 [a]	56.0	15.7	0.39	
0.45 [a]	28.0	3.1	0.31	
0.5 [a]	22.0	2.4	0.26	
0.4 [b]	28.0		0.54	4.5
0.37 ($H=0$ T) [c]	85.0		0.54	4.5
0.37 ($H=8$ T)	400.0		0.16	18.0

[a]From Ref. 3
[b]From Ref. 6
[c]Our sample.

specific heat, arising from phonons. A part of the T^3 contribution to C_p can also arise from AFM spin waves.

The T^3 contribution is likely to be enhanced over and above the actual Debye contribution because of the presence of AFM spin waves, since our COI sample has canted AF order in this temperature range. The results of fitting the data to the above equation are shown in Table I. The parameters obtained by us are very similar to that seen by Lees *et al.*[6] In Table I we have collected the parameters from different published data for comparison.

However, the interesting question is whether in a magnetic field of 8 T where the COI is melted into a FMM phase can we see the appearance of a linear specific heat term. In a past investigation on polycrystalline samples of $La_{0.5}Ca_{0.5}MnO_3$ in a magnetic field of 8.5 T (Ref. 17) (which is high enough to melt the COI state) no linear term had been observed. The issue of absence of the linear term in the FMM phase obtained after melting the COI state is thus real, particularly when one compares it with the low-temperature specific heat of the FMM phase as seen in the CMR region, $\gamma \approx 7.8$ mJ/mol K^2 in $La_{0.8}Ca_{0.2}MnO_3$ (Ref. 18) and 5.2 mJ/mol K^2 in $La_{0.7}Ca_{0.3}MnO_3$ (Ref. 19).

C_p/T vs T^2 for our sample in presence of an 8 T magnetic field is shown in Fig. 12. The specific heat data have been fitted using Eq. (1), with the parameters as shown in Table I. Interestingly, the specific heat in the presence of a magnetic field is distinctly lower than the specific in 0 T for all T <40 K. Lowering of the specific heat in the presence of a magnetic field has been reported Smolyaninova *et al.*[3] Since resistivity measurements indicate the sample to be in a metallic state, one would expect an extra linear term appearing in the Eq. (1) in the presence of a magnetic field. As seen in Fig. 12, we could not detect the presence of any linear term even in presence of 8 T. From the uncertainty in the data we find an upper limit of $\gamma \lesssim 0.1$ mJ/mol K^2, which is too small.

It is apparent from Table I, that contribution of the β_3 term is halved in the presence of a magnetic field. This appears to be the main reason for lower C_p in $H=8$ T compared to that in the absence of a magnetic field. This can be explained as follows. The T^3 term contains an additional

antiferromagnetic spin-wave contribution for the COI sample. For an antiferromagnetic spin-wave spectrum where $E=Dq$, the magnetic contribution to the specific heat is $\propto T^3$. The melting of the COI state to a FMM state leads to a collapse of this AFM order and thus there will be no AFM spin-wave contribution to the specific heat. This would result in a decrease of the T^3 term. However, the presence of FM order should give a ferromagnetic spin-wave contribution $\propto T^{3/2}$. We have attempted fitting a $T^{3/2}$ term to the 8 T specific heat data. However, we could not detect any $T^{3/2}$ term. Thus, it appears that the specific heat as observed in the presence of a magnetic field does not have a ferromagnetic spin-wave contribution. (Note) that we do not attach much significance to the change in the β_5 term as observed. Neither do we interpret it as a change in the lattice contribution. The apparent large change in β_5 may be an artifact of fitting because the β_5 term being small in $H=0$ T data, it is difficult to fix it. Also the data at $H=8$ T show a small extra contribution above 6 K which is included in the fit β_5 term but it may not have anything to do with it.)

Briefly, we find that the specific heat at low temperature needs more investigation in single-crystalline CO systems and in a high magnetic field. The existing data (which includes too few single-crystal data) both in zero field and magnetic field (high enough to melt the CO state) do not allow us to reach many definite conclusions other than the fact that in the FMM phase obtained by melting the COI state in a high magnetic field does not have a large enough γ that is comparable to FMM phases seen in manganites showing CMR behavior.

CONCLUSION

Our study of the specific heat in a CO system done over an extended temperature range of 3–300 K in the presence of 0 and 8 T magnetic field gives us much useful and new information regarding the thermodynamics of the CO transition. This paper gives a clear measurement of the entropy in a single-crystal and also the latent heat (at T_{CO}) in zero field and in a magnetic field. The latent heat released proves the strong first-order nature of the transition, which had never been shown to be so in actual measurements of the specific heat. An estimate of the numbers like the latent heat in 0 and 8 T fields sets clearly the bound and scale within which any theoretical models must work. It is a very important number for any phase transition which gives the CO transition (in both 0 and 8 T) a thermodynamic basis. Important also is the observation of a finite entropy change at the CO melting in a magnetic field. The result shows that a small but finite and qualitative difference in entropy exists between the FMM phase and the CI phase at the melting transition in a magnetic field where the former (FMM) phase (which is the low-T phase) has a lower entropy than the other phase (which is the high-T phase). Interesting also is the smallness of the entropy.

The low-temperature $C_p(T<15$ K) show no linear dependence on T as expected from an insulating sample.

Surprisingly, this electronic term is absent even when the COI state is melted to a FMM state by a 8 T magnetic field. An attempt had been made to understand the observed discrepancy between the specific heat of a single-crystal and a polycrystalline sample in the low-temperature regime.[20–26]

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