PHYSICAL REVIEW B, VOLUME 63, 224403

# Low-temperature specific heat in $Pr_{0.63}Ca_{0.37}MnO_3$: Phase separation and metamagnetic transition

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(Received 21 December 2000; published 8 May 2001)

The application of a sufficiently large magnetic field in $Pr_{0.63}Ca_{0.37}MnO_3$ can enforce a ferromagnetic state, resulting in an ‘‘insulator-metal’’ transition owing to both actuation of double-exchange mechanism and charge-order melting. In the present study, the low-temperature magnetoelectronic state of this compound has been investigated by specific-heat measurements. It was shown that the metamagnetic transition has clear signatures in specific-heat data. Combination of specific heat, magnetization, and resistivity measurements allowed us to propose a comprehensive picture of the hysteretic features around this transition in the frame of a field-dependent phase-separation scenario. A more quantitative analysis also gave strong support to the percolative nature of the magnetoresistive transition in this compound.

DOI: 10.1103/PhysRevB.63.224403 PACS number(s): 75.30.Vn, 65.40.Ba, 75.30.Ds

## I. INTRODUCTION

The existence of electronic phase separation[1,2] in manganites is a feature that strongly influences most of their properties. Owing to various phenomena such as double exchange[3] and charge ordering,[4,5] the electronic and magnetic properties are strongly correlated to each other in these materials.[6,7] Most often, the ferromagnetic (FM) and antiferromagnetic (AFM) states are associated with highly conductive and insulating behaviors, respectively. Subdivision in domains of both of these states can make the overall behavior particularly sensitive to the application of a magnetic field. By promoting spin alignment, an external magnetic field indeed affects directly the energy balance between both states, and can thus modify their volumic ratio. Thereby, phase-separation phenomena[8,9] are deeply involved in metamagnetic transitions leading to colossal magnetoresistivity (CMR) in manganese oxides.[10]

Compounds of the system $Pr_{1-x}Ca_xMnO_3$ with $x$ close to 0.4 are known to exhibit such a metamagnetic transition under not too high magnetic fields.[11–14] Furthermore, $Pr_{0.6}Ca_{0.4}MnO_3$ is a well-documented material on which extensive investigations have been carried out by magnetic and resistivity measurements,[15–17] as well as by neutron-diffraction experiments.[5,9,18]

The present study is focused on the low-temperature range where CMR occurs, combining specific-heat measurements under magnetic fields $C(T,H)$ with more standard magnetization $M(T,H)$ and resistivity $\rho(T,H)$ measurements. Specific heat is a thermodynamic quantity, which is complementary to magnetization and resistivity in many aspects. It is indeed a bulk property (unlike resistivity for which percolation can be dominant),[2,8,19] which has not the ‘‘vectorial’’ character of magnetization (in which, what is actually measured is the average projection of the magnetic moments along one direction).

The paper is organized as follows. In Sec. II, some experimental details are given about the samples and the measuring techniques. Section III contains a brief overview of the main properties of the studied compound. Section IV is devoted to the analysis of the low-temperature specific-heat data under zero field, while Sec. V addresses $C$-vs-$T$ curves recorded under field. Section VI reports an experimental investigation and a comparative study of the metamagnetic transition on the basis of magnetization, resistivity, and specific-heat measurements. Section VII is focused on the analysis of the hysteretic behaviors around this transition in the frame of a phase-separation scenario. In Sec. VIII, a quantitative analysis of $C$-vs-$H$ and $M$-vs-$H$ curves is proposed to account for the critical field value observed in $\rho$-vs-$H$. Section IX points out the main results and their implications.

## II. EXPERIMENTAL DETAILS

Using the floating-zone method with a feeding rod of nominal composition $Pr_{0.6}Ca_{0.4}MnO_3$, a several-cm-long single crystal was grown in a mirror furnace. Two samples were cut out of the central part of this crystal, one of them for resistivity measurements and the other for magnetization and specific-heat measurements. X-ray diffraction and electron diffraction (ED) studies, which were performed on pieces coming from the same part of the crystal, attested that the samples are single phased, homogeneous, and well crystallized. The reconstruction of the reciprocal space confirmed the expected $Pnma$-type orthorhombic cell at room temperature, with $a_0 \simeq a_p\sqrt{2}$, $b_0 \simeq 2a_p$, and $c_0 \simeq a_p\sqrt{2}$ ($a_p$ is the parameter of the cubic perovskite cell). The ED investigation also showed the existence of twinning domains, which result from the reversible phase transitions (from cubic to orthorhombic) undergone by the crystals upon cooling. Therefore, all physical measurements performed on such samples are averaged over the six oriented domains coexisting in the $Pnma$ phases. The cationic composition derived from energy-dispersive x-ray microanalyses leads to the formula $Pr_{0.63}Ca_{0.37}MnO_3$.

Specific-heat measurements were carried out by means of a commercial set up (quantum design) using the two-$\tau$ relax-

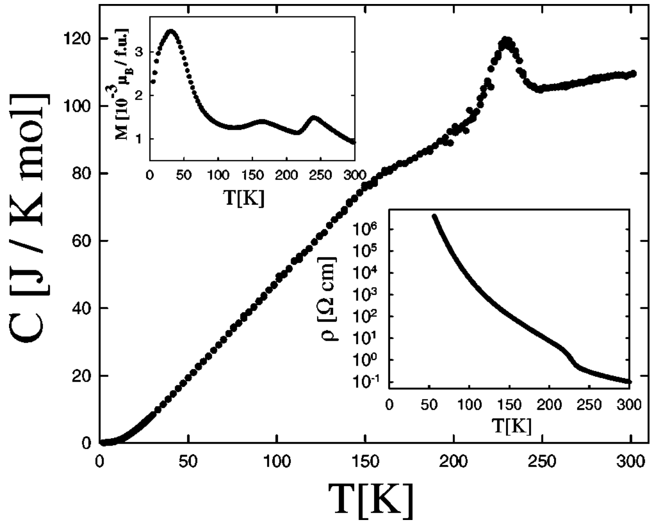

FIG. 1. Temperature dependence of specific heat under zero field in $Pr_{0.63}Ca_{0.37}MnO_3$ (main panel), together with magnetization (upper inset) and resistivity (lower inset) under 100 G and 0 G, respectively.

ation method, at temperatures from 2.2 to 300 K and under magnetic fields up to 9 T. The sample mass was 0.0414 g. The background signal, including the exact amount of Apiezon *N* used to paste the sample on the platform, was recorded in a first run and it was then subtracted from the total heat capacity. The absence of any significant field dependence of this background signal was carefully checked in the low-temperature range (2.2–15 K). The accuracy of the specific-heat data in this temperature range was also verified by measuring a 99.999% pure copper sample.

Resistivity measurements were performed by the standard four-probes technique, at temperatures from 5 to 300 K and fields up to 9 T. Magnetization measurements were recorded by using a superconducting quantum interference device magnetometer at temperatures from 5 to 300 K and fields limited to 5 T.

## III. BASIC FEATURES

The temperature dependence of the specific heat $C$, the magnetization $M$ and the resistivity $\rho$, up to 300 K and under zero (or low) field, is shown in Fig. 1. These results are in remarkable agreement with previous studies carried out on $Pr_{0.6}Ca_{0.4}MnO_3$.[15,16,18,20]

The $M(T)$ curve measured under 100 G after zero-field cooling exhibits three peaks. According to neutron-diffraction studies,[5,11,18] the two peaks around 230 and 160 K correspond to the establishment of a charge ordering ($T_{CO}$) and to an antiferromagnetic-spin ordering ($T_N$), respectively. In compounds close to ours, this antiferromagnetic order among the Mn spins was found to be of the pseudo-CE (charge exchange)-type.[21,22] As the temperature is further decreased, one observes that the magnetization starts increasing below 100 K, then it exhibits a peak around 30 K and it finally decreases as approaching 5 K. We observed that the fall in magnetization below 30 K is much less pronounced if the sample is cooled under field, a behavior that suggests the existence of magnetic frustration in this very low-temperature range. In some previous studies on related compounds, the increase in magnetization that takes place below about 100 K was ascribed to the development of a spin canting in the antiferromagnetic structure.[11,18] In terms of phase separation, this behavior can alternatively be accounted for by the appearance of a small amount of ferromagnetic domains dispersed in a collinear antiferromagnetic matrix.[22] It must be emphasized that the low-temperature value of $M$, which is presently observed (some $10^{-3}\mu_B$/f.u.), remains very small as compared to those encountered in compounds of slightly different compositions, which are known to behave as bulk ferromagnets[17] (e.g., some $10^{-1}\mu_B$/f.u. in $Pr_{0.8}Ca_{0.2}MnO_3$ under 100 G). Such a result is consistent with the fact that the AFM order remains largely predominant in our $Pr_{0.63}Ca_{0.37}MnO_3$ samples at low temperatures. The $\rho(T)$ curve in zero field displays a pronounced semiconductinglike behavior, leading to an insulating state at low temperature. One can also denote a clear kink around 230 K, which is related to the charge-ordering phenomenon.

The most salient feature of the $C(T)$ curve under zero field is a prominent peak around $T_{CO}$. It must be pointed out that the large amplitude of this peak is not only related to the entropy change associated with charge and orbital ordering, but also to the related structural distortion.[22] There is a remarkable quantitative agreement about the $T_{CO}$ values, if one compares the peak temperature in $C(T)$ at 229 K with the midpoints of the jumps observed in $\rho(T)$ and $M(T)$, at 227 and 228 K, respectively. The $C(T)$ curve also displays a knee around 150 K that can be correlated to $T_N \simeq 160$ K shown in $M(T)$. It was found that both peaks observed in $C(T)$ are shifted to lower temperatures upon application of a large magnetic field (e.g., by 10 and 15 K under 9 T, for $T_{CO}$ and $T_N$, respectively). The high-temperature regime in $C(T,H)$ will be addressed elsewhere. Let us here focus on the low-$T$ range where CMR effects take place.

## IV. SPECIFIC HEAT IN ZERO FIELD

Figure 2 shows an enlargement of the $C(T)$ curve below 15 K under zero field. Relevant contributions to specific heat in this low-$T$ range are (i) a phononic term $C_{lat}$ related to lattice vibrations, (ii) a hyperfine term $C_{hyp}$ related to level splitting induced by large local magnetic fields at the Mn and Pr nuclear spins, (iii) a linear in temperature term $C_\gamma$ related to free charge carriers or to disorder effects, and (iv) a magnetic term $C_{mag}$ related to spin waves. As mentioned above, the volumic fraction of the FM phase in zero field is so small that its contribution to specific heat can be neglected. At very low temperatures, i.e., $T < 10$ K, $C_{lat}$ can be fairly approximated by a $T^3$ term. For extensions of the low-$T$ range up to 15 K, it is generally required to add a correction in the form of a $T^5$ term. In the absence of an upturn in $C(T)$ at lowest temperatures, $C_{hyp}$ can be approximated by the high-$T$ tail of a Schottky function, leading to a $T^{-2}$ term.[23] Owing to the strong insulating character observed at low temperatures under zero field, one can assume there is no electronic term related to free charge carriers. On the other hand, recent stud-

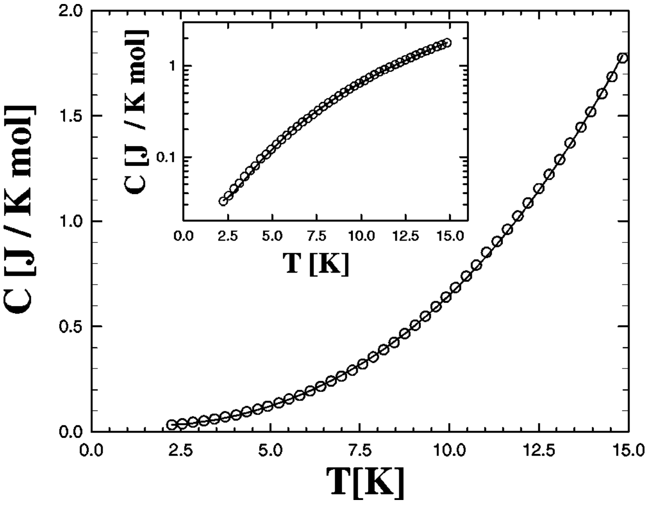

FIG. 2. Low-temperature enlargement of the $C$-vs-$T$ curve under zero field. Solid line is a fit to the data with Eq. (4.1) when considering $\gamma=0$ and $n=2$ (see text). Inset shows the same results in semilogarithmic scales. Note that a fitting curve of comparable quality is also found when choosing $\delta=0$ and $\gamma\neq 0$ (see text).

ies on insulating manganites have reported the occurrence of large $\gamma$ values related to disorder effects that can affect spin and/or charge degrees of freedom.[24,25] As for $C_{mag}$, the case of spin-wave excitations in a pseudo-CE-type antiferromagnet has not yet been theoretically investigated. Predictions are just available for more standard magnetic structures, such as ferromagnetic, isotropic antiferromagnetic, and layered antiferromagnetic states, for which $C_{mag}$ varies as $T^{3/2}$, $T^3$, and $T^2$, respectively.[23,26] We have chosen for $C_{mag}$ an approximation in the form $\delta T^n$, $n>0$ being an undefined parameter. Adding these various contributions, the temperature dependence of the specific heat in $\mathrm{Pr_{0.63}Ca_{0.37}MnO_3}$ at low $T$ can be expressed in the form

$$C=\alpha T^{-2}+\gamma T+\beta_3 T^3+\beta_5 T^5+\delta T^n. \tag{4.1}$$

Reliable results cannot be expected by directly using such an expression with six free parameters. In a first step, one can limit the temperature range investigated in order to reduce the number of parameters. In the range 5–10 K, the influences of both hyperfine term and $\beta_5 T^5$ correction can fairly be neglected, leading to the simplified expression $C=\beta_3 T^3+\gamma T+\delta T^n$. Even doing so, the fitting process does not converge to a unique set of parameters. Accordingly, we have first considered the extreme situations corresponding to either $\delta=0$ or $\gamma=0$. A very good fit is obtained in the former case with $\beta_3=0.54$ mJ/K$^4$ mol and $\gamma=11$ mJ/K$^2$ mol. In this temperature range, a $C/T$ versus $T^2$ plot clearly appears as a straight line that does not extrapolate to zero. However, it must be noticed that the ‘‘background’’ curve ($\beta_3 T^3+\gamma T$), obtained by applying the above parameters over the entire temperature range, strongly departs from the data in the high-$T$ side (10–15 K), a feature that implies the existence of a particularly large $\beta_5 T^5$ correction (see below). The fits obtained with the alternative approach ($\beta_3 T^3+\delta T^n$) are a little less good in the 5–10 K range. On the other hand, they are much less sensitive to moderate extensions of the fitting range. As a matter of fact, if one considers the range 5–12 K, a better fit is obtained with $\beta_3 T^3+\delta T^2$ than with $\beta_3 T^3+\gamma T$. Actually, the best results involve combinations of $\gamma T$ and $\delta T^n$ terms, the best values of $n$ lying in the range 1.5–2 (for $\gamma=0$) and 2–2.5 (for $\gamma\neq 0$). At this step, one can already state that no unambiguous conclusion can be drawn about the exact values of these parameters. Let us proceed with the analysis of the ‘‘boundary’’ situations: $\gamma\neq 0$ with $\delta=0$, or $\gamma=0$ with $\delta\neq 0$. We chose $n=2$ in the latter case to be comparable with the previous study of Lees *et al.*[20] Using the ‘‘background’’ functions derived from the analysis of the intermediate-$T$ range, we address the residual data $C_{res}=C-(\beta_3 T^3+\gamma T+\delta T^n)$ calculated over the whole temperature range. This residual data is fitted to the remaining terms of Eq. (4.1), $C_{res}=\alpha T^{-2}+\beta_5 T^5$. Both $\alpha$ and $\beta_5$ can be unambiguously determined since they are associated with very contrasted temperature dependences. As in the first step, the fits were performed with a data weighting equal to $1/C$, consistent with the experimental uncertainty. In the case $\gamma=0$ with $n=2$, the best set of parameters is $\beta_3=0.34$ mJ/K$^4$ mol, $\beta_5=-0.01$ $\mu$J/K$^6$ mol, $\delta=3.1$ mJ/K$^3$ mol, and $\alpha=70$ mJ K/mol. In the case $\delta=0$, one finds $\beta_3=0.54$ mJ/K$^4$ mol, $\beta_5=-0.2$ $\mu$J/K$^6$ mol, $\gamma=11$ mJ/K$^2$ mol, and $\alpha=4$ mJ K/mol. The mean errors ($\Delta C/C$) over the whole temperature range are 1.6% and 1.4% for the former and latter cases, respectively. These results are illustrated in Fig. 2 by the fitting curve corresponding to $\gamma=0$, shown in linear and semilogarithmic scales (note that both fitting curves described above would appear to be nearly superimposed in such plots). In both cases, the $\beta_3$ parameters are significantly larger than those usually associated with lattice contribution (0.1—0.2 mJ/K$^4$ mol).[24,26–29] It is likely that a part of the cubic term originates from spin-wave excitations (pseudo-CE-type AFM).[20] This excess in $\beta_3$ is more pronounced when fitting without a $T^2$ term. The $\delta$ value (3.1 mJ/K$^3$ mol) found with $\gamma=0$ is comparable to that reported by Lees *et al.* in $\mathrm{Pr_{0.6}Ca_{0.4}MnO_3}$ with the same analysis ($\delta=1.89$ mJ/K$^3$ mol).[20] Furthermore, the rather large $\gamma$ value (11 mJ/K$^2$ mol) found with $\delta=0$ is consistent with values found in insulating manganites, including $\mathrm{Pr_{0.65}Ca_{0.35}MnO_3}$.[24,25] The $\beta_5$ term is particularly large for $\delta=0$, more than one order of magnitude larger than for $\gamma=0$. The most surprising point is the very low value $\alpha=4$ mJ K/mol associated with $\delta=0$. The hyperfine term related to Mn only yields $\alpha$ values larger than 8 mJ K/mol.[26] Furthermore, large values ranging between 30 and 60 mJ K/mol have been previously reported for $\mathrm{Pr_{1-x}Ca_xMnO_3}$ with $x$ close to 0.4.[20,25] The $\alpha$ value found with $\gamma=0$ is more compatible with these results.

We have mainly discussed above the boundary cases, $\gamma=0$ or $\delta=0$. Actually, all intermediate situations lead to satisfying fits to the data. In this case, all parameters $\alpha,\beta_3,\beta_5,\gamma$, and $\delta$ take intermediate values. The value of $n$ can vary between about 1.5 and 2.5. It is obvious that the present low-$T$ specific-heat measurements cannot allow us to

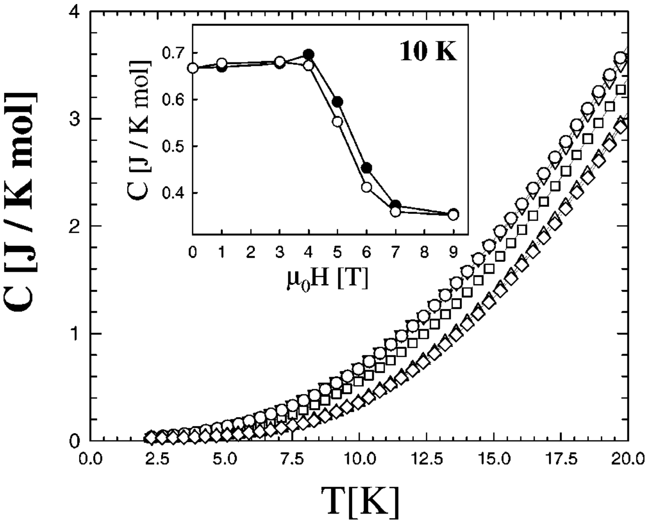

FIG. 3. $C$-vs-$T$ curves under various fields, recorded in the FC mode [0 T (○); 3 T (∇); 5 T (□); 7 T (Δ); 9 T (◇)]. Inset displays specific-heat values at 10 K, inferred from $C$-vs-$T$ scans: FC mode (○) and ZFC mode (●).

determine a unique set of values for all parameters involved in Eq. (4.1). In insulating AFM compounds like $Pr_{1-x}Ca_xMnO_3$ with $x \sim 0.4$, the occurrence of $\gamma T$ and/or $\delta T^n$ terms is a point of active debate. Relevant pieces of information that can be drawn from the present study are (i) we observed that the data can be reasonably fitted with either $\gamma = 0$ or $\delta = 0$, but the most plausible solution is a combination of both contributions; (ii) the upper limit for the $\gamma$ value, which is related to disorder effects in the present case, is 11 $mJ/K^2$ mol; (iii) the best $n$ values ranges between 1.5 and 2.5., with $n = 2$, the upper limit for $\delta$ is 3.1 $mJ/K^3$ mol; and (iv) the magnetic contribution associated with spin-wave excitations in a pseudo-CE-type AFM has a temperature dependence that may be accounted for by a combination of $T^3$ and $T^n$ terms, with $n$ close to 2.

## V. SPECIFIC HEAT UNDER FIELD

Let us now investigate the influence of magnetic field on $C$-vs-$T$ curves at low temperatures. Figure 3 shows such curves for five fields between 0 and 9 T. These data were registered upon warming the sample that was previously cooled under field (FC mode). One observes that the curves for fields up to 3 T remain almost superimposed to the one at zero field. For 5 T, a noticeable downward shift of the $C(T)$ curve takes place. This field effect is further pronounced for 7 T, before showing a trend to saturation under 9 T. The overall behavior is a bit more complex at very low temperatures ($T < 5$ K) owing to the enhancement of the hyperfine contribution with magnetic field. Apart from this very low-$T$ range, the field effect is qualitatively the same in the range 5—15 K.

Let us choose for instance $T = 10$ K to investigate more precisely the magnetic field influence. The inset of Fig. 3 shows $C$-vs-$H$ plots at $T = 10$ K derived from $C$-vs-$T$ curves under field. Together with data extracted from FC curves (like those of the main panel), we have also plotted data taken from curves recorded after zero-field cooling down to 2 K (ZFC mode). The most salient feature emerging from these plots is a pronounced step located around 5 T. The curves are nearly flat below 4 T, and they also tend to saturate on a plateau above 7 T. In other respects, one observes a small shift (by about 10%) between the ZFC and FC curves in the transition regime.[30]

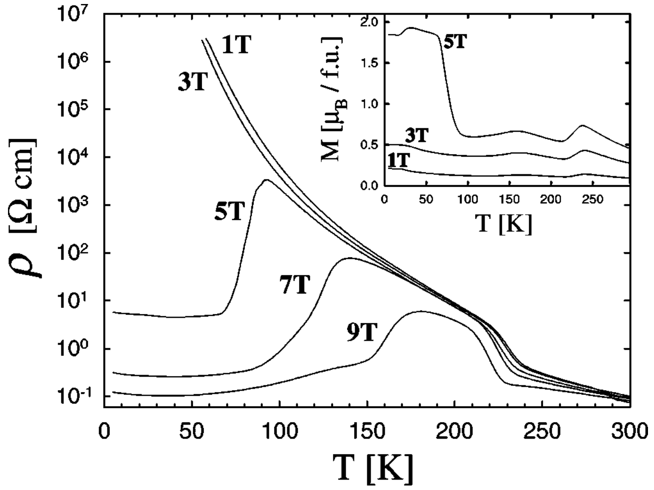

FIG. 4. Temperature dependence of resistivity (main panel) and magnetization (inset), under various magnetic-field values (FC mode).

Two recent studies in related compounds reported similar field effects on $C$-vs-$T$ curves. In $Pr_{0.65}Ca_{0.35}MnO_3$, Smolyaninova *et al.*[25] observed that the curve under 8.5 T lies much below the one under zero field, while Roy *et al.*[31] reported a progressive downward shift of the curves for fields equal to 3, 6, and 9 T in $Pr_{0.7}Ca_{0.3}MnO_3$.

## VI. METAMAGNETIC TRANSITION

The existence of a metamagnetic transition around 5 T in compounds close to $Pr_{0.6}Ca_{0.4}MnO_3$ has already been revealed by several techniques other than specific heat.[15] Figure 4 displays resistivity and magnetization measurements recorded in the FC mode. Among the $\rho(T)$ curves of the main panel, one observes a striking contrast between the curves for $\mu_0 H \leqslant 3$ T (which keep the insulating character previously shown in zero field) and those for $\mu_0 H \geqslant 5$ T (which display a high conductive state below a field-dependent temperature). Under 5 T, this characteristic temperature is around 90 K and the transition is quite sharp. As the field is increased, this transition broadens while shifting to higher temperatures. For $T < 50$ K, the field effect on resistivity is so large that one can talk about ''colossal'' magnetoresistance.

The inset shows $M(T)$ curves for different fields up to 5 T (the highest available field in our magnetometer). For $T \geqslant 100$ K, one observes that the magnetization is roughly proportional to the field. This property persists at low temperatures for $\mu_0 H \leqslant 3$ T. Under larger fields, the situation drastically changes. For 5 T, one observes a sudden increase

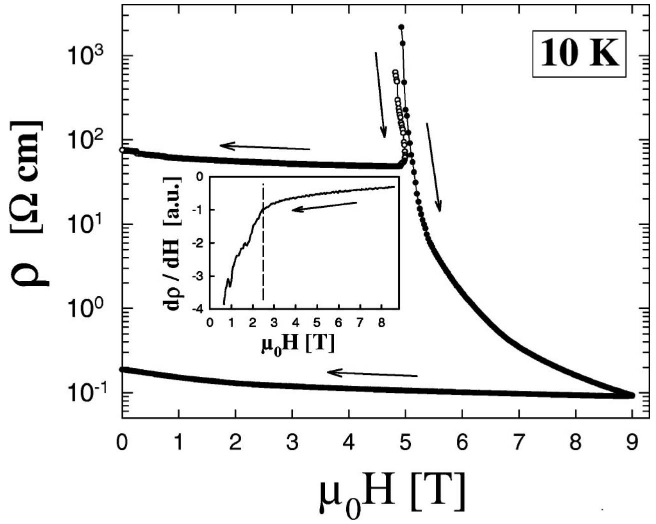

FIG. 5. Resistivity at 10 K recorded in two field sweeps [0 T →5 T→0 T (○) and 0 T→9 T→0 T (●)], after a zero-field cooling. Inset shows the derivative of $\rho$-vs-$H$ along the reverse branch 9 T→0 T. The dashed line denotes the change of regime around 2.5 T (see text).

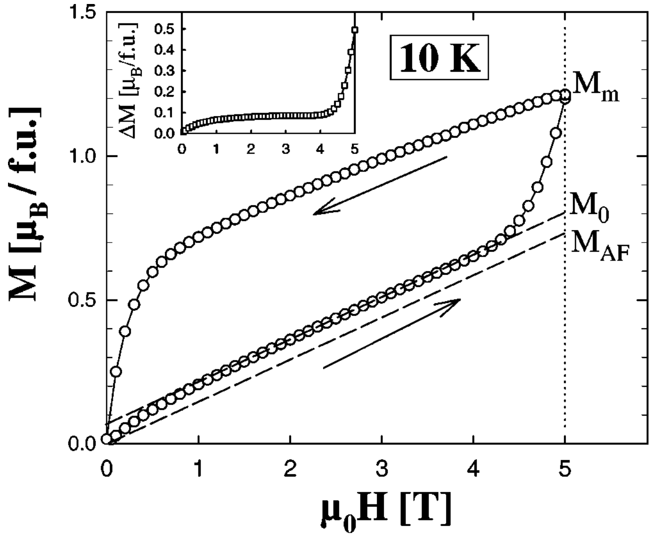

FIG. 6. Magnetization loop (0 T→5 T→0 T) at 10 K, recorded after zero-field cooling. Various characteristic values of magnetization under 5 T are also shown (see text). Inset shows the ''ferromagnetic part'' of the virgin magnetization branch (see text).

in magnetization at $T \leqslant 90$ K, i.e., the same temperature as the one marking the drop in resistivity. The magnetization at low temperatures under 5 T reaches a rather large value, which represents a substantial fraction of the expected value for a full polarization of the Mn spins ($\simeq 3.63\mu_B$/f.u.). It must be also noted that one observes a downward step by about $0.1\mu_B$/f.u. below 20 K, which may be related to magnetic ordering in the Pr sublattice. Only neutron-diffraction studies could clearly answer this question. Beyond this peculiarity, the most important point emerging from the inset of Fig. 4 is that a substantial ferromagnetic component appears at low temperatures in $\mathrm{Pr_{0.63}Ca_{0.37}MnO_3}$ for $\mu_0 H \geqslant 5$ T.

This metamagnetic transition can be more suitably investigated on the basis of $\rho$-vs-$H$ and $M$-vs-$H$ measurements. Let us consider the case of $T=10$ K as previously done for specific heat. Figure 5 shows $\rho(H)$ at 10 K, starting from a ZFC state. Two field scans have been recorded: 0 T→9 T →0 T and 0 T→5 T→0 T. In accordance with the behavior displayed in Fig. 4, the resistivity is so high at low fields that it cannot be measured. Approaching 5 T, both curves exhibit a steep fall in $\rho$. The slight shift between them can be ascribed to the larger time constant used in the 0 T →5 T→0 T scan (e.g., at 10 K and under 5 T after a zero-field cooling, $\rho$ is divided by a factor 3 between 1 and 10 min). As the field approaches 9 T, one observes in our semilogarithmic plot that the decrease in resistivity seems to saturate. This behavior indicates that the metamagnetic transition that starts around 5 T is essentially achieved under 9 T. This transition is found to be highly irreversible.[15] The reverse branches of $\rho(H)$ are nearly flat as the field is turned back to zero. This results in a giant hysteresis at low fields, down to $H=0$. This behavior is qualitatively the same in both scans, though the metamagnetic transition in the minor loop is far from being completed. The inset shows a crossover in the resistivity variation as the field is decreased from 9 to 0 T, which will be discussed in the next section. These $\rho(H)$ curves show that the application of a high enough field at low temperatures leads to a state of strongly reduced resistivity that behaves as a *deeply frozen metastable state*, nearly insensitive to a subsequent field nulling.

Figure 6 shows $M$-vs-$H$ measurements at 10 K recorded after a zero-field cooling. Along the virgin magnetization branch, $M$ first increases smoothly up to 4 T. Then, a much more pronounced increase takes place between 4 and 5 T, a crossover that reveals the starting of the metamagnetic transition. In a closer inspection of the low-field range ($\mu_0 H \leqslant 4$ T), one can also detect a rounding of $M$ vs $H$ below about 1 T. The overall shape of the first magnetization branch below 4 T can thus be seen as the superimposition of a ferromagnetic component (yielding the rounding of the curve at low fields) and of an antiferromagnetic component (associated with the linear in $H$ dependence at intermediate fields). The relevancy of such a scheme was recently supported by combined nuclear magnetic resonance and magnetization measurements in $\mathrm{(La_{0.25}Pr_{0.75})_{0.7}Ca_{0.3}MnO_3}$.[32] The inset shows the data after subtraction of the antiferromagnetic contribution, inferred from the slope of $M(H)$ around 3 T. The ferromagnetic part of $M$ obtained in this way ($\Delta M$ displayed in the inset of Fig. 6) appears as the sum of a zero-field component, whose saturation value is about $0.09\mu_B$/f.u., and of a field-induced component rising for $\mu_0 H > 4$ T. As the field is reduced from 5 T, the magnetization exhibits a strong hysteretic behavior in the largest part of the field range. However, below about 0.5 T, $M$ starts decreasing more rapidly and it goes to zero for $H=0$. This behavior cannot be related to the partial character of the transition induced by a maximum field of 5 T. Indeed Lees *et al.*[15] also noted this behavior in their study of $\mathrm{Pr_{0.6}Ca_{0.4}MnO_3}$ up to 12 T at 10 K. This feature observed in

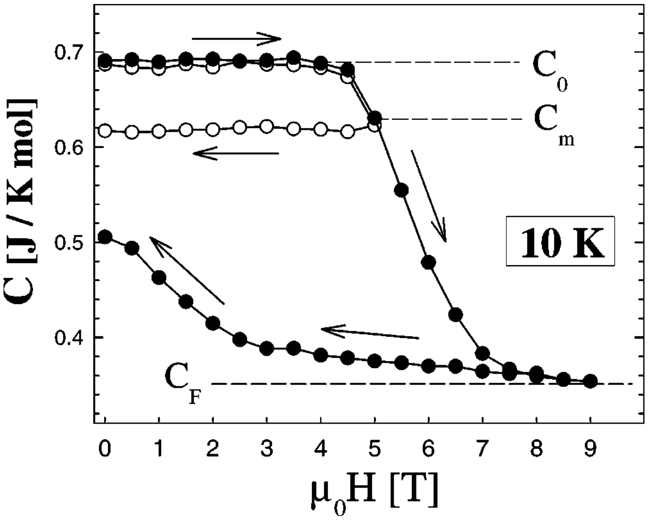

FIG. 7. Specific heat at 10 K as a function of magnetic field. Two runs have been registered after zero-field cooling: 0 T →5 T→0 T (○) and 0 T→9 T→0 T (●). The field sweep directions are indicated by arrows. Various characteristic values are also shown (see text).

magnetic measurements is in sharp contrast with the giant hysteresis observed down to 0 in $\rho$ vs $H$.

Actually, it is well known that resistivity and magnetization measurements probe the sample state in different ways. In particular, resistivity is very sensitive to percolation, a phenomenon of great importance in materials able to undergo electronic phase separation.[2] In contrast, magnetization is really a bulk quantity, averaging the local properties over the whole sample volume. It must be pointed out, however, that what is averaged is the projection of the local moments onto one particular direction (most often the direction of the applied field as in our case). As a consequence, it is in principle impossible to distinguish, at low fields, a perfect antiferromagnet from a ferromagnet consisting of completely disoriented domains. Specific heat is also a bulk, averaged quantity, but it does not have the above-mentioned vectorial character of magnetization. In specific-heat measurements, the contributions of all the regions or domains simply add to each other. Such measurements can thus be complementary to resistive and magnetic studies.

## VII. HYSTERESIS IN *C*-versus-*H*

We carried out $C$-vs-$H$ measurements at $T=10$ K. Two scans were recorded: 0 T→9 T→0 T and 0 T→5 T →0 T. In both cases, the measurements were started after a zero-field cooling procedure. The results are shown in Fig. 7. Along the scan 0 T→9 T, $C$-vs-$H$ exhibits a striking step-like shape,[33] which is very similar to the reconstruction shown in the inset of Fig. 3. The transition starts for fields larger than 4 T and saturates approaching 9 T. According to the $M(H)$ measurements at 10 K recorded by Lees *et al.* in a very close compound,[15] our sample is expected to be transformed into a completely ferromagnetic state under 9 T. The reversibility observed in Fig. 7 between 8 and 9 T lends further support to the fact that the transition is nearly complete in this field range. In contrast, the transition is clearly incomplete in the minor loop up to 5 T. In both cases, however, very pronounced hysteretic behaviors are observed.

The reverse branch 5 T→0 T exhibits a remarkable flat aspect. In terms of field-induced transformation from antiferromagnetic to ferromagnetic order, this means that all the FM domains created by the application of 5 T persist when the field is turned back to zero. Such a proof of complete hysteresis down to zero in the 0 T→5 T→0 T scan demonstrates that the observed absence of remanent magnetization actually results from a complete disorientation between the FM domains. It is worth noticing that this disorientation has no drastic effect on resistivity. Actually, we are just dealing here with a disorientation between domains, each of them being ferromagnetically well ordered. In addition, this disorientation may be small between adjacent domains, which limits the effects on resistivity via the double-exchange mechanism.

The down-sweep process in the scan 0 T→9 T→0 T is more complex than in the previous case. Two regimes have to be distinguished: (i) as $H$ is decreased from 9 T down to about 2.5 T, $C$ smoothly increases; (ii) then, below 2.5 T down to 0 T, a much larger slope is observed. One remarks that this crossover value of 2.5 T is close to the field at which the magnetization starts to drop from its saturated value in the $M(H)$ measurements up to 12 T carried out by Lees *et al.*[15] In their experiment, this first drop is followed by a steeper regime at low fields, which can be ascribed to a disorientation effect as discussed above. The combination of those magnetization data with our specific-heat measurements leads us to propose the following scenario:

(1) After application of 9 T, the sample becomes completely ferromagnetic. As $H$ is reduced down to about 2.5 T, the reverse leg of $M(H)$ is essentially flat,[15] showing that the sample remains in a complete ferromagnetic state. As for the weak field dependence of $C$ which is observed above 2.5 T, it can be accounted for by the standard influence of $H$ on the spin-wave contribution in ferromagnets. The magnitude of this field-induced stiffening of the spin waves ($\simeq -1.8\%$ $T^{-1}$) is indeed consistent with what we observed in ferromagnetic compounds such as $Pr_{0.8}Ca_{0.2}MnO_3$ ($\simeq -2.1\%$ $T^{-1}$). Such a field effect is not observed on the reverse leg of the scan 0 T→5 T→0 T. In this case, just a part of the sample has been driven in the ferromagnetic state. As shown by the $\rho(H)$ curve, the volumic fraction of conductive FM phase under 5 T is just at the percolation threshold. One can thus assume the presence of small FM domains only partly connected to each other. This granular FM structure inhibits the development of low-energy (long-wavelength) spin waves, contrary to the case of the bulk ferromagnet induced by 9 T. Therefore the contribution of ferromagnetic spin waves may be negligible along the scan 0 T→5 T→0 T.

(2) Below 2.5 T, the magnetization significantly decreases (under fields that are not small enough to invoke disorientation effects), while the specific heat increases much more rapidly than can be accounted for by the spin-wave field dependence. Therefore one has to consider that, in this regime, a part of the sample is progressively turned back into the AFM state. Since the volumic fraction of FM phase re-

mains well above the percolation threshold, resistivity is not drastically affected. One can denote, however, a larger slope $d\rho/dH$ around 2.5 T on the branch 9 T→0 T (see inset of Fig. 5).

(3) Below about 0.5 T, the magnetization vectors of the FM domains that are still present are no longer aligned to each other. The macroscopic magnetization progressively vanishes as the field is reduced to zero, while there is no spectacular change in specific heat.

In conclusion, one can remark that the metamagnetic transformation between AFM and FM ordering is totally irreversible when it is incomplete (0 T→5 T→0 T), whereas it is only partly irreversible when it is complete (0 T→9 T→0 T). It looks like there was a limit value for the remanent ferromagnetic fraction.

## VIII. PERCOLATION THRESHOLD

One can estimate the volumic fraction ($x$) of ferromagnetic phase induced by the application of 5 T on the basis of magnetization and specific-heat measurements. For both quantities, the mixed state that takes place under 5 T allows us to write

$$M_m=(1-x)M_{AFM}+x\,M_{FM}, \tag{8.1}$$

$$C_m=(1-x)C_{AFM}+x\,C_{FM}, \tag{8.2}$$

where $M_m$ and $C_m$ are the measured values under 5 T; $M_{FM}$ and $C_{FM}$ are the magnetization and specific-heat values in the complete ferromagnetic state, respectively; $M_{AFM}$ and $C_{AFM}$ are the magnetization and specific-heat values in the complete antiferromagnetic state, respectively.

It must be noted that the above relation about magnetization involves the reasonable assumption that all ferromagnetic domains are aligned with the external field under 5 T. For $C_{FM}$, let us consider the value toward which tends the specific heat at 9 T (see Fig. 7), while $M_{FM}$ is taken as the expected value for a fully Mn spin-polarized phase, i.e., about $3.63\mu_B$/f.u.. The situation is more complex for $C_{AFM}$ and $M_{AFM}$ because of the small ferromagnetic fraction ($x_0$) already present in zero field, which requires to be corrected for the low-field values $C_0$ and $M_0$ (see Figs. 6 and 7). $M_{AFM}$ is the magnetization under 5 T if the whole sample was in the AFM state. It can thus be inferred from the extrapolation at 5 T of the low-field range ($M_0\simeq 0.79\mu_B$/f.u.) after subtraction of the magnetization associated with the zero-field ferromagnetic component (see Fig. 6). One estimates $x_0\simeq(M_0-M_{AFM})/M_{FM}\simeq 0.02$. This value can then be used to evaluate $C_{AFM}$ from a relation similar to Eq. (8.2):

$$C_0=(1-x_0)C_{AFM}+x_0C_{FM}. \tag{8.3}$$

Finally, the volumic fraction of ferromagnetic phase at 5 T can be derived in two ways: first, from magnetization via the relation

$$x_M=\frac{M_m-M_{AFM}}{M_{FM}-M_{AFM}}, \tag{8.4}$$

second, from specific heat via the relation

$$x_C=\frac{(C_0-C_m)+x_0(C_m-C_{FM})}{(C_0-C_{FM})}. \tag{8.5}$$

With $M_m\simeq 1.22\mu_B$/f.u., $M_{AFM}\simeq 0.72\mu_B$/f.u., $M_{FM}\simeq 3.63\mu_B$/f.u., $C_m\simeq 0.630\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $C_F\simeq 0.355\ \mathrm{J\,K^{-1}\,mol^{-1}}$, $C_0\simeq 0.685\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and $x_0\simeq 0.02$, one obtains $x_M\simeq 0.17$ and $x_C\simeq 0.18$. There is a remarkable quantitative agreement between both values, even though they are derived from essentially independent measurements. If one neglects the small ferromagnetic component in the low-field state (i.e., assuming $M_{AFM}\approx M_0$ and $C_{AFM}\approx C_0$), one obtains similar results: $x_M\simeq 0.15$ and $x_C\simeq 0.17$.

In $Pr_{0.63}Ca_{0.37}MnO_3$, the AFM matrix is highly insulating (charge-ordered), while the FM domains have a rather low resistivity related to double exchange. The $\rho(H)$ curves at 10 K display a percolationlike transition around 5 T (see Fig. 5). Whatever the details of the analysis, the volumic fraction of conducting domains under 5 T is always found to be in remarkable accord with the theoretical predictions for a three-dimensional (3D) percolation threshold ($\simeq 17\%$).[34] Closely related results have been recently reported in the system $La_{5/8-x}Pr_xCa_{3/8}MnO_3$, by varying the FM fraction via the Pr content.[8] Such behaviors are strong supports to the relevancy of percolation effects connected to a field-dependent phase separation in manganese oxides exhibiting colossal magnetoresistivity.[19]

## IX. CONCLUSION

In $Pr_{0.63}Ca_{0.37}MnO_3$, a real-space charge-ordering followed by an AFM spin ordering (pseudo-CE-type) takes place below about 230 and 160 K, respectively. Both characteristic temperatures can be detected in magnetization, resistivity, and specific-heat curves. Upon further cooling below 100 K, a tiny ferromagnetic component appears, which can be related to an incipient-phase-separation phenomenon. In addition to lattice and hyperfine terms, the low-$T$ dependence of specific heat in zero field can be well accounted for by considering either a large $\gamma T$ term related to disorder, a $\delta T^n$ term ($n$ close to 2) possibly related to spin-wave excitations in a pseudo-CE-type AFM, or most likely a combination of both contributions.

$Pr_{0.63}Ca_{0.37}MnO_3$ undergoes a metamagnetic transformation around 5 T at low temperature, yielding a marked increase in magnetization accompanied by a steep fall in resistivity. We have shown that this transition also manifests itself as a sudden decrease in $C(H)$ around 5 T. In a zero-field-cooling curve, specific heat is nearly unchanged up to 4 T (essentially AFM state), while it tends to saturate under 9 T (fully FM state), giving rise to an amazing steplike shape of $C$-vs-$H$. Specific heat can also provide us with additional information about irreversibility effects in the metamagnetic transition. For instance, one can easily distinguish a disorientation among FM domains from a reverse transformation back to the AFM state. The combination of $C(H)$, $M(H)$, and $\rho(H)$ data allowed us to propose an overall description of the various hysteretic behaviors observed by these different techniques, pointing out the determinant influence of the maximum field applied to the system.

## ACKNOWLEDGMENTS

The authors thank L. Hervé (CRISMAT, Caen) for the crystal growth, M. Hervieu for electron microscopy investigations, and C. Marcenat for information about specific-heat calibration.

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[1] S. Mori, C.H. Chen, and S.-W. Cheong, Phys. Rev. Lett. **81**, 3972 (1998); G. Allodi, R. De Renzi, F. Licci, and M.W. Pieper, *ibid.* **81**, 4736 (1998); A. Moreo, S. Yunoki, and E. Dagotto, Science **283**, 2034 (1999).

[2] M. Uehara, S. Mori, C.H. Chen, and S.-W. Cheong, Nature (London) **399**, 560 (1999).

[3] C. Zener, Phys. Rev. **82**, 403 (1951); P.W. Anderson and H. Hasegawa, *ibid.* **100**, 675 (1955); P.-G. de Gennes, *ibid.* **118**, 141 (1960).

[4] E.O. Wollan and W.C. Koehler, Phys. Rev. **100**, 545 (1955); J.B. Goodenough, *ibid.* **100**, 564 (1955).

[5] Z. Jirák, S. Krupička, Z. Šimša, M. Dlouhá, and S. Vratislav, J. Magn. Magn. Mater. **53**, 153 (1985).

[6] Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **74**, 5108 (1995).

[7] P. Schiffer, A.P. Ramirez, W. Bao, and S.-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).

[8] K.H. Kim, M. Uehara, C. Hess, P.A. Sharma, and S.-W. Cheong, Phys. Rev. Lett. **84**, 2961 (2000).

[9] C. Frontera, J.L. García-Muñoz, A. Llobet, M. Respaud, J.M. Broto, J.S. Lord, and A. Planes, Phys. Rev. B **62**, 3381 (2000).

[10] S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen, Science **264**, 413 (1994); R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, Phys. Rev. Lett. **71**, 2331 (1993).

[11] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, J. Phys. Soc. Jpn. **65**, 1043 (1996).

[12] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Morimoto, and Y. Tokura, Phys. Rev. B **53**, R1689 (1996).

[13] J.M. De Teresa, M.R. Ibarra, C. Marquina, P.A. Algarabel, and S. Oseroff, Phys. Rev. B **54**, R12 689 (1996).

[14] M. Tokunaga, N. Miura, Y. Tomioka, and Y. Tokura, Phys. Rev. B **57**, 5259 (1998).

[15] M.R. Lees, J. Barratt, G. Balakrishnan, D.McK. Paul, and M. Yethiraj, Phys. Rev. B **52**, R14 303 (1995).

[16] A. Maignan, C. Martin, F. Damay, and B. Raveau, Z. Phys. B: Condens. Matter **104**, 21 (1997).

[17] C. Martin, A. Maignan, M. Hervieu, and B. Raveau, Phys. Rev. B **60**, 12 191 (1999).

[18] M.R. Lees, J. Barratt, G. Balakrishnan, D.McK. Paul, and C. Ritter, Phys. Rev. B **58**, 8694 (1998).

[19] A. Anane, J.-P. Renard, L. Reversat, C. Dupas, P. Veillet, M. Viret, L. Pinsard, and A. Revcolevschi, Phys. Rev. B **59**, 77 (1999).

[20] M.R. Lees, O.A. Petrenko, G. Balakrishnan, and D.McK. Paul, Phys. Rev. B **59**, 1298 (1999).

[21] H. Yoshizawa, H. Kawano, Y. Tomioka, and Y. Tokura, Phys. Rev. B **52**, R13 145 (1995).

[22] D.E. Cox, P.G. Radaelli, M. Marezio, and S.-W. Cheong, Phys. Rev. B **57**, 3305 (1998).

[23] E.S.R. Gopal, *Specific Heat at Low Temperatures* (Plenum, New York, 1966).

[24] L. Ghivelder, I. Abrego Castillo, M.A. Gusmão, J.A. Alonso, and L.F. Cohen, Phys. Rev. B **60**, 12 184 (1999).

[25] V.N. Smolyaninova, A. Biswas, X. Zhang, K.H. Kim, B.-G. Kim, S.-W. Cheong, and R.L. Greene, Phys. Rev. B **62**, R6093 (2000).

[26] B.F. Woodfield, M.L. Wilson, and J.M. Byers, Phys. Rev. Lett. **78**, 3201 (1997).

[27] J.J. Hamilton, E.L. Keatley, H.L. Ju, A.K. Raychaudhuri, V.N. Smolyaninova, and R.L. Greene, Phys. Rev. B **54**, 14 926 (1996).

[28] L. Ghivelder, I. Abrego Castillo, N.McN. Alford, G.J. Tomka, P.C. Riedi, J. MacManus-Driscoll, A.K.M. Akther Hossain, and L.F. Cohen, J. Magn. Magn. Mater. **189**, 274 (1998).

[29] T. Okuda, Y. Tomioka, A. Asamitsu, and Y. Tokura, Phys. Rev. B **61**, 8009 (2000).

[30] In the FC mode, the system *feels* the field at high temperature, which can facilitate the development of the metamagnetic transition.

[31] M. Roy, J.F. Mitchell, A.P. Ramirez, and P. Schiffer, Phys. Rev. B **62**, 13 876 (2000).

[32] A. Yakubovskii, K. Kumagai, Y. Furukawa, N. Babushkina, A. Taldenkov, A. Kaul', and O. Gorbenko, Phys. Rev. B **62**, 5337 (2000).

[33] Related magnetocaloric effects in field sweeps at low temperature have recently been reported in $Pr_{0.7}Ca_{0.3}MnO_3$ by M. Roy *et al.* in Ref. 30.

[34] H. Scher and R. Zallen, J. Chem. Phys. **53**, 3759 (1970); S. Kirkpatrick, Rev. Mod. Phys. **45**, 574 (1973).