Calorimetric and magnetic investigations of the metamagnet $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$

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The antiferromagnetic, charge and orbitally ordered (AFCOO) ground state of some manganites like $Pr_{0.5}Ca_{0.5}MnO_3$ can be efficiently destabilized by slight Mn-site substitutions. Such a weakened AFCOO state and related disorder effects were investigated in $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$ by combining specific-heat and magnetization measurements. The study was extended to the ferromagnetic state which can be installed in this compound by field application at low T. Under a large field, the temperature-driven collapse of this ferromagnetic state was found to be consistent with the Clausius-Clapeyron relation typical of first-order transitions. A comparative study of the various magnetoelectronic states encountered in the substituted and unsubstituted compounds was also carried out by investigating the low-temperature dependence of specific heat.

I. INTRODUCTION

Mixed-valent perovskite manganites of formulation $R_{1-x}A_x MnO_3$ (R and A being a trivalent rare-earth and a divalent alkaline-earth ion, respectively) have attracted considerable interest in the recent years owing to the great variety of fascinating properties they can exhibit.[1] In particular, for x values around 0.5, a charge and orbital ordering (COO) can take place among the Mn^{3+} ($t_{2g}^3 e_g^1$) and Mn^{4+} ($t_{2g}^3 e_g^0$) species, accompanied by an antiferromagnetic (AF) ordering of CE type.[2,3] This AFCOO magnetoelectronic state is particularly robust in the compound $Pr_{0.5}Ca_{0.5}MnO_3$, owing to its small average A-site cationic radius. At low temperatures, very high magnetic fields larger than 20 T are required to collapse this state via a metamagnetic transition.[4] On the other hand, small substitution levels on the Mn site were shown to be very efficient to destabilize this AFCOO state.[5] While the Mn^{4+}/Mn^{3+} ratio remains close to 1 in such $Pr_{0.5}Ca_{0.5}Mn_{1-y}M_y O_3$ (M being the substituting element), the AFCOO state is drastically weakened. In addition, the metamagnetic transition at very low temperatures in such materials was found to develop in a very peculiar way. Indeed, for a great variety of M cations and over a rather large y range around 0.03, the magnetization, resistivity, and specific heat curves at low T display a succession of abrupt jumps as a function of magnetic field.[6,7]

The aim of the present work is to investigate in more details this peculiar magnetoelectronic state, by studying the T dependence of specific heat and magnetization. For this purpose, we chose the composition $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$ which combines two particular characteristics: (i) there is no detectable ferromagnetic component in the ground state obtained after zero-field cooling; (ii) full Mn-spin polarization can be reached under our maximum magnetic field (9 T). All the properties of the weakened AFCOO $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$ [hereafter denoted as (PrCa50)Ga5%] were systematically compared to those of the pure, strong AFCOO $Pr_{0.5}Ca_{0.5}MnO_3$ [hereafter denoted as PrCa50]. In (PrCa50)Ga5%, the metamagnetic transition resulting from application of 9 T at low T was shown to lead to the ferromagnetic (F) state. It was also found that

(PrCa50)Ga5% remains in this F state when the field is subsequently decreased to zero. These features allowed us to investigate (PrCa50)Ga5% in two very different magnetoelectronic states: namely, the disordered AFCOO state and the F state.

The paper is organized as follows. Experimental details are given in Sec. II. In Sec. III, the nature of the disordered AFCOO ground state of (PrCa50)Ga5% is discussed by comparing specific heat and magnetization measurements to those recorded in the pure AFCOO state of PrCa50. Section IV reports on the installation and properties of the field-induced F state in (PrCa50)Ga5%, on the basis of magnetization measurements. Section V is devoted to the analysis of the specific-heat data in the high-T range. This part is focused on the entropy change found at the Curie temperature of the F state under high field. The relevance of the Clausius-Clapeyron equation to this transition is investigated by combining specific-heat and magnetization measurements. Section VI is devoted to the specific-heat data in the low-T range. A comprehensive analysis is presented for a set of measurements recorded in PrCa50 and (PrCa50)Ga5%, corresponding to various magnetoelectronic states (AFCOO, disordered AFCOO, and F). The question of the excess specific heat found in some AFCOO manganites is addressed. Section VII is a summary of the main results, with some concluding remarks.

II. EXPERIMENTAL DETAILS

Ceramic samples were prepared according to standard procedures.[6] Both specific-heat and magnetization measurements were carried out in a Physical Properties Measurement System (Quantum Design), with magnetic fields up to 9 T and temperatures down to 2.2 K. Specific-heat measurements are derived from a relaxation method with a two-τ analysis, while magnetization measurements are performed with an extraction method. In (PrCa50)Ga5%, specific-heat and magnetization curves versus temperature were recorded in three different conditions: under zero or low field, after a zero-field cooling (hereafter denoted as [ZFC-0T]); under 9 T, after zero-field cooling and field application at low temperature
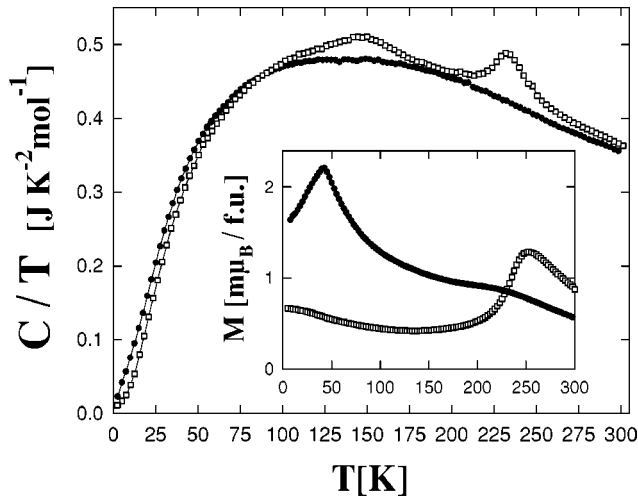
FIG. 1. Specific heat of $Pr_{0.5}Ca_{0.5}MnO_3$ (open squares) and $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$ (solid circles), recorded upon warming under 0 T after zero-field cooling (ZFC). The inset shows magnetization recorded upon warming under 0.01 T after ZFC, in the same compounds.

(hereafter denoted as [ZFC-9T]); under zero or low field, after zero-field cooling and field cycling 0 T–9 T–0 T at low temperature (hereafter denoted as [REM-0T]). In each case, the measurements were collected upon warming. Curves labeled [ZFC-0T] and [REM-0T] were recorded under 0 T in the case of specific-heat data, while they were recorded under 0.01 T in the case of magnetization data. This small field was applied to the remanent magnetization ([REM-0T]) in order to favor the alignments of the F domains and to be directly comparable with [ZFC-0T]. In the compounds of the present study, we emphasize that such a small field (0.01 T) does not affect at all the magnetoelectronic state, which is still the same as under 0 T.

III. DISORDERED AFCOO STATE INDUCED BY Mn-SITE SUBSTITUTIONS

The main panel of Fig. 1 displays C/T-vs-T curves under zero field in PrCa50 and (PrCa50)Ga5%. The inset shows $M(T)$ curves in the same samples, recorded under a small field (0.01 T) after zero-field cooling (ZFC). The $C/T(T)$ of PrCa50 exhibits two peaks at $T_{COO} \simeq 235$ K (setting up of the charge and orbital ordering) and $T_N \simeq 150$ K (setting up of the antiferromagnetic spin ordering), values in good agreement with those previously obtained by other techniques.[3,4,8,9] With a phenomenological background line consisting of a polynomial fitting of the $C/T(T)$ curve well away from the peaks, one can get a rough estimate of the entropy changes at each transition. This yields $\Delta S(T_{COO}) \simeq 1.4$ J K^{-1} mol^{-1} and $\Delta S(T_N) \simeq 0.8$ J K^{-1} mol^{-1}, values in line with previous results in close compounds.[10,11] While T_N is hardly visible on the $M(T)$ curve of PrCa50, T_{COO} manifests itself as a prominent peak. There is very good accordance between the temperature of highest slope in $M(T)$ and the temperature of the peak in $C(T)$.

In (PrCa50)Ga5%, there is no clear evidence of T_{COO} or

T_N on the $C(T)$ curve. On the $M(T)$ curve, however, one can still observe a spreading kink around 220 K, indicative of a smooth setting up of COO. This result is consistent with electron microscopy investigations at low T (92 K), which attested to the establishment of short-range COO in this compound.[6] A neutron diffraction study in a related compound [(PrCa50)Al5%], which exhibits the same macroscopic features, also revealed the persistence of a bulk AF order of CE type in such compounds.[12] Like for COO, a more progressive and short-range character of the magnetic ordering might explain the absence of visible signature on $C(T)$. The most striking feature in (PrCa50)Ga5% is the existence of a prominent peak centered at $T_p \simeq 45$ K on the $M(T)$ curve. As previously reported, this cusp is a common property of $Pr_{0.5}Ca_{0.5}Mn_{1-y}M_yO_3$ compounds, which indicates a spin-glass or cluster-glass-like behavior.[7] Indeed, there is a pronounced divergence between low-field ZFC and FCC (field-cooled-cooling) curves below T_p in dc measurements, while T_p clearly increases with frequency in ac measurements.[7] In the case of (PrCa50)Ga5%, the relative variation of T_p per frequency decade is equal to 0.017, a value consistent with spin- or cluster-glass behaviors.[13] Although this peak must be related to some disorder among the spin interactions, a precise microscopic description is still lacking. Similar problems also exist in some manganites without Mn-site substitutions.[14,15]

Turning back to the main panel of Fig. 1, one can see that the $C(T)$ curves of PrCa50 and (PrCa50)Ga5% are never superimposed onto each other, in any temperature range. Actually, there is a crossing between these curves around 90 K. The upper location of the (PrCa50)Ga5% curve at low T corresponds to an easier entropy release, a behavior qualitatively consistent with the whole disorder affecting all degrees of freedom in this Mn-site-substituted sample. Accordingly, the curve of (PrCa50)Ga5% can be expected to lie below that of PrCa50 in the intermediate-T range containing the T_{COO} and T_N of the latter compound. More surprising is the persistence of a shift between the two curves up to 300 K, i.e., in a regime where both samples are supposed to be in a similar paramagnetic, charge-disordered state. The Mn-sublattice disordering may affect the phonon spectrum and thus the lattice contribution, but more subtle effects can also be in play, such as the existence of large polaronic excitations in the case of the "pure" PrCa50.

IV. FERROMAGNETIC STATE INDUCED BY FIELD APPLICATION AT LOW T

A. Field-driven transformation from the disordered AFCOO state to the F state

The above-mentioned peculiar metamagnetic behavior of the $Pr_{0.5}Ca_{0.5}Mn_{1-y}M_yO_3$ compounds is illustrated in the inset of Fig. 2 by the $M(H)$ curve of (PrCa50)Ga5% recorded at 5 K after ZFC. Following a low-field linear regime consistent with AF ordering, the metamagnetic transition develops through a salient succession of three abrupt steps. Under 9 T, the magnetization is that expected for full Mn-spin polarization.[16] As the field is decreased, the curve exhibits a nearly flat shape, revealing a strongly irreversible behavior.
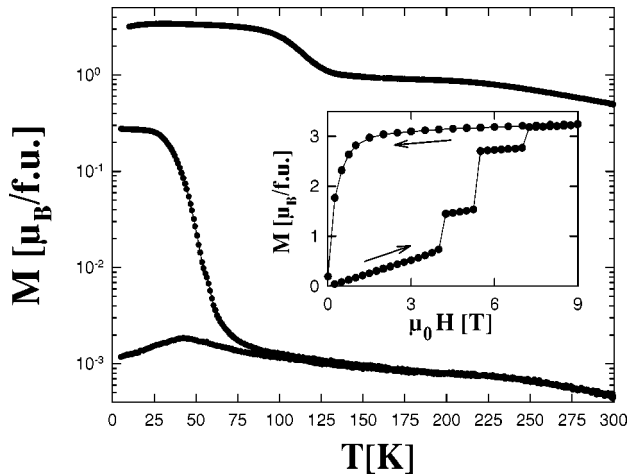
FIG. 2. Magnetization curves of $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$, recorded upon warming under three different conditions (from bottom to top): under 0.01 T after ZFC ([ZFC-0T] state), under 0.01 T after a 0-T–9-T–0-T cycling at 5 K ([REM-0T] state), and under 9 T after ZFC ([ZFC-9T] state). Note the logarithmic scale of the vertical axis. The inset shows the hysteresis loop recorded at 5 K after ZFC in this compound.

The magnetization decrease when approaching zero field can be ascribed to a standard effect of disorientation between ferromagnetic domains. If the field is reincreased from zero, one gets a curve perfectly superimposed on the reverse leg of the first loop (not shown here for the sake of clarity). This whole behavior indicates that we are dealing with a totally irreversible transition, which was also supported by the perfectly horizontal shape of the reverse leg of $C(H)$ loops.[6] One can thus state that, once 9 T has been applied at low T, (PrCa50)Ga5% is irreversibly switched to a ferromagnetic state (F state). As long as the temperature is not increased, the sample remains in this F state whatever the field value, in particular even under zero field.

B. Temperature dependence of the magnetization in the disordered AFCOO and the F states

The above-discussed metamagnetic properties of (PrCa50)Ga5% offer the interesting opportunity to study a same sample in very different magnetoelectronic states. Accordingly, $M(T)$ curves were recorded in the three different conditions described in Sec. II: [ZFC-0T] (disordered AF-COO state without field), [ZFC-9T], and [REM-0T] (field-induced ferromagnetic state, under field or not, respectively). These three curves are shown in Fig. 2 in a semilogarithmic plot.

A striking point emerging from this figure is the great difference between the two curves recorded under the same low field (0.01 T). At low T, the magnetization of [REM-0T] is rather constant and it is more than two orders of magnitude larger than that of [ZFC-0T] (this latter curve being the one displayed in the inset of Fig. 1). Then, the [REM-0T] curve exhibits a steep fall around 40 K, before smoothly merging on the [ZFC-0T] curve above 75 K. Such an overall behavior is consistent with the ferromagnetic nature of the [REM-0T]

state. Accordingly, the temperature of the fall in magnetization can be regarded as the *intrinsic Curie temperature* of the field-induced ferromagnetism in (PrCa50)Ga5%. We speculate that this $T_c \simeq 40$ K is a characteristic of the Mn sublattice in half-doped (Pr,Ca)MnO$_3$ compounds; i.e., the Ga substitution just comes into play to reveal this underlying interaction usually hidden by COO in the "pure" Mn compounds.[7] One can also note that this T_c has a value very close to that of T_p seen in the [ZFC-0T] curve. This is consistent with the fact that the development of F interactions competing with the weak AF "background" is at the origin of the glasslike behavior found in [ZFC-0T].

The magnetization of [ZFC-9T] remains very close to the saturation value over a wide temperature range, before undergoing a sizable decrease around 110 K. As those recorded under 0.01 T, the curve under 9 T then exhibits a smooth kink around 220 K related to COO. Consistently with our analysis of [REM-0T], the temperature of 110 K can be seen as the Curie temperature under 9 T. Owing to an additional Zeeman energy under 9 T, the ferromagnetic ordering can indeed be sustained up to larger temperatures. It must be pointed out, however, that the present influence of the magnetic field noticeably differs from what is observed in most standard ferromagnets, in that one observes a strong shift of T_c without significant broadening of the transition. Similar field effects were found in some intrinsically ferromagnetic manganites such as $La_{1-x}Ca_xMnO_3$ with x close to 0.3.[17] This peculiarity was recently ascribed to the unusual first-order character of the ferromagnetic transition in some manganites, a feature which might itself be related to low values of the tolerance factor.[18]

V. ANALYSIS OF SPECIFIC-HEAT DATA IN THE HIGH-T RANGE

Specific-heat measurements $C(T)$ were carried out in the same three states ([ZFC-0T], [REM-0T], and [ZFC-9T]) as those previously investigated by $M(T)$ curves. At low T, the three curves exhibit a complex behavior detailed in Sec. VI. Above about 130 K, all three curves are well superimposed up to 300 K. Actually, the most striking feature is found in the intermediate-temperature range, when comparing [ZFC-9T] to both [ZFC-0T] and [REM-0T].

A. Temperature-driven collapse of the F state under high field

Figure 3(a) shows an enlargement of this region in a C/T-vs-T plot. A clear peak emerges from the [ZFC-9T] curve around 110 K, which can be related to the thermally induced collapse of the ferromagnetic order. The effective width of this peak (75–130 K) can be directly estimated from the merging points on both "0 T" curves. The superimposition of the [ZFC-0T] and [REM-0T] curves in this T range also allows us to use them as a relevant background line to estimate the entropy change around T_c (9 T). Integration of the difference of C/T between [ZFC-9T] and both other curves in the range 75–130 K yields $\Delta S \simeq 0.9$ J K^{-1} mol^{-1}.
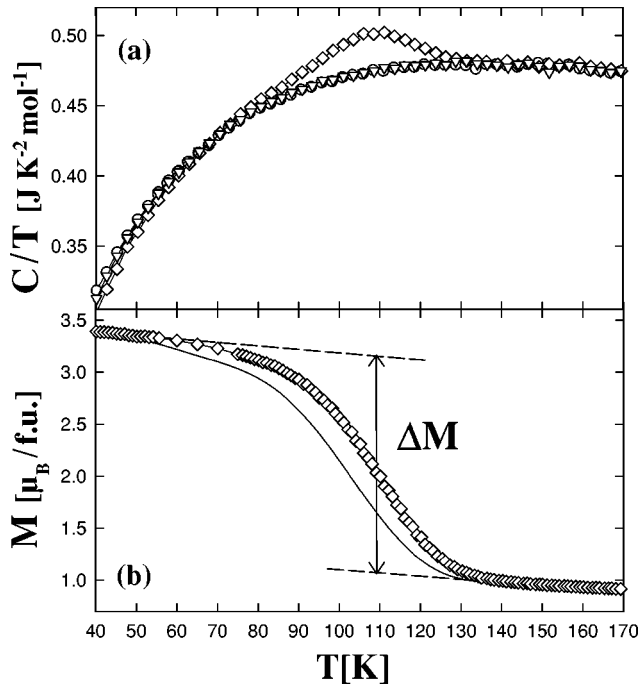
FIG. 3. Specific-heat and magnetization curves in $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$. The upper panel (a) displays specific-heat data measured upon warming in three different states (see text): [ZFC-0T] (circles), [REM-0T] (triangles), and [ZFC-9T] (diamonds). The lower panel (b) displays magnetization data measured under 9 T in two different modes: ZFC mode, i.e., in the [ZFC-9T] state (diamonds), and in the field-cooling (FC) mode (solid line). Also shown in (b) the construction used to derive the magnetization jump ΔM.

The expected ΔS at a ferromagnetic-paramagnetic transition under zero field is $R\ln(2S+1)$, S being the spin value. Under large magnetic fields, the entropy of the paramagnetic state is decreased, but this effect is negligibly small here because of the high temperature. In (PrCa50)Ga5%, the fractions of $Mn^{3+}(S=2)$ and $Mn^{4+}(S=3/2)$ are 0.47 and 0.53, respectively, leading to a theoretical ΔS value equal to $12.4\ J\,K^{-1}\,mol^{-1}$, much larger than the experimental one.

It must be kept in mind, however, that the interplay between various degrees of freedom which takes place in manganites can make the situation more complex. In particular, because of the double-exchange mechanism,[19] there is an intimate relationship between magnetic and electronic properties. As a matter of fact, the magnetic transition at $T_c = 110$ K also separates a charge-delocalized regime ($T < T_c$) from a partly charge-ordered state ($T > T_c$). This means that the electronic entropy *decreases* as T is increased across T_c. This contribution, opposite to that coming from the magnetic entropy, results in a decrease of the effective ΔS measured by the specific heat. The order of magnitude of this effect can be approximated by $\Delta S(T_{COO})$ in PrCa50 or by the integral $\int_0^{T_c}(\gamma T / T)dT$, taking for the electronic linear term some values typical of metallic manganites ($\gamma \sim 4\ mJ\,K^{-2}\,mol^{-1}$).[20] It turns out that such corrections ($<2\ J\,K^{-1}\,mol^{-1}$) are not large enough to account for the low experimental ΔS value.

Actually, even in the simplest ferromagnetic transitions in manganites, the experimental ΔS are always found to be much lower than the theoretical ones. For instance, ΔS values close to $1.5\ J\,K^{-1}\,mol^{-1}$ were found in $Pr_{0.6}(Ca,Sr)_{0.4}MnO_3$ and ΔS close to $1.9\ J\,K^{-1}\,mol^{-1}$ in $La_{0.67}Ca_{0.33}MnO_3$, i.e., less than 15% of the expected values.[10,21] Such discrepancies, quantitatively in line with our result, are generally ascribed to substantial entropy release out of the T_c region.[10]

Beyond this quantitative aspect, it must be pointed out that the [ZFC-9T] curve in Fig. 3(a) clearly displays an entropy change associated with the collapse of a field-induced ferromagnetic order. This question was recently investigated by Raychaudhuri *et al.*[11] in $Pr_{0.63}Ca_{0.37}MnO_3$ by measuring $C(T)$ under a field of 8 T, for which there is a ferromagnetic, conducting state at low T. Around the metal-insulator transition corresponding to the collapse of the ferromagnetic order, these authors observed on the $C(T)$ curve two diplike anomalies well separated in temperature. It must be emphasized that these features are qualitatively very different from our observations.

B. Relationship between specific-heat and magnetization measurements

Figure 3 displays a clear correlation between the $C(T)$ and $M(T)$ curves of [ZFC-9T], the temperature of the peak in $C(T)$ well coinciding with the temperature of the highest slope in $M(T)$. As previously discussed, this characteristic temperature ($\simeq 110$ K) corresponds to the Curie temperature of the F phase of (PrCa50)Ga5% under 9 T. Magnetization curves under 9 T were recorded upon heating (ZFC) and upon cooling (FC). As shown in Fig. 3(b), both curves exhibit a clear step around $T_c(9T)$. There is a shift between the two curves, the midpoint of the transition for decreasing temperature (FC) lying about 7 K below the one obtained when increasing temperature (ZFC). However, it must also be noticed that the ZFC and FC curves are well superimposed on each other, apart from this transition regime ($T<50$ K and $T>140$ K), indicating that the transition takes place within a reversible regime. Thus, thermodynamic relationships can be expected to be reasonably valid for such a transition.

A first-order transition is characterized by discontinuities in the first derivatives of the free energy (like magnetization and entropy). In "real" samples, some inhomogeneities can transform such discontinuities into more or less rounded steps, as those presently found. The shift observed between the ZFC and FC curves is also consistent with an underlying first-order transition, since a thermal hysteresis is generally observed in such transitions (as a consequence of the metastability of the domain of coexistence between the two phases).[22]

In a first-order transition, there is an expected correlation between the entropic and magnetic jumps, given by the Clausius-Clapeyron equation. In practical units, this relation can be written as

$$\Delta S(J\,K^{-1}\,mol^{-1}) \simeq -5.585\,\frac{\Delta M(\mu_B\,/\,f.u.)}{\dfrac{dTc}{dB}\,(K\,/\,T)}. \quad (1)$$
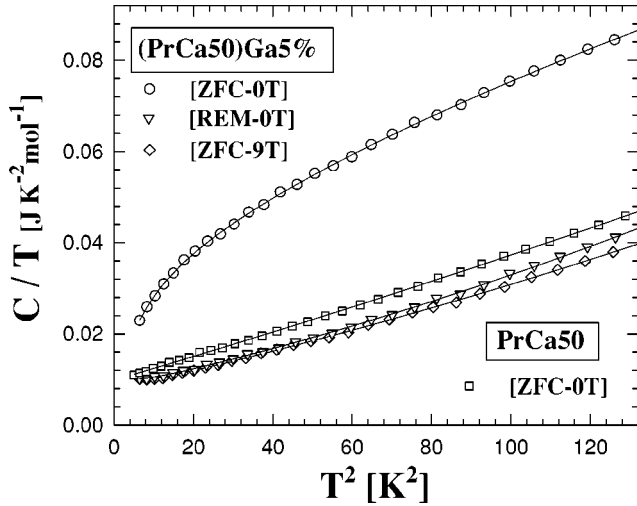
FIG. 4. C/T-vs-T^2 plots of the low-T specific heat in $Pr_{0.5}Ca_{0.5}MnO_3$ (PrCa50) and $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$ [(PrCa50)Ga5%]. The measurements in (PrCa50)Ga5% were recorded upon warming under three different conditions: under 0 T after ZFC ([ZFC-0T] state), under 0 T after a 0-T–9-T–0-T cycling at 2.2 K ([REM-0T] state), and under 9 T after ZFC ([ZFC-9T] state). The lines are fitting curves corresponding to the parameters given in Table I (first set of parameters in the case of (PrCa50)Ga5% [ZFC-0T]).

The T_c values under 9 T, 8 T, and 7 T were derived from the point of highest slope in $M(T)$ curves (ZFC). Using a phenomenological quadratic fitting, the derivative dT_c/dB around the point (9 T, 110 K) was estimated to be 9.61 K/T. As illustrated in Fig. 3(b), the magnetization jump ΔM was approximated by the difference between linear, parallel extrapolations of the $M(T)$ curve below and above the transition regime ($T < 60$ K and $T > 130$ K), leading to $\Delta M \simeq 2.07 \mu_B$/ f.u. Using Eq. (1), one obtains an equivalent entropy jump $\Delta S \simeq 1.2$ J K^{-1} mol^{-1}, in reasonable agreement with the value $\Delta S \simeq 0.9$ J K^{-1} mol^{-1} directly derived from calorimetric measurements.

VI. ANALYSIS OF SPECIFIC-HEAT DATA IN THE LOW-T RANGE

Let us now turn to the very low-T regime ($T < 12$ K). Figure 4 displays the specific heat of (PrCa50)Ga5% in the states [ZFC-0T], [REM-0T], and [ZFC-9T], along with that of PrCa50 recorded under 0 T after ZFC ([ZFC-0T] state). All fits to data were performed over the range 2.2–12 K, with a weighting inversely proportional to $C(T)$.

A. $Pr_{0.5}Ca_{0.5}MnO_3$: AFCOO state under 0 T

Let us start the analysis with the [ZFC-0T] curve of PrCa50, which can be regarded as typical of a pure AFCOO state under zero field. One observes that the C/T-vs-T^2 plot of this curve exhibits a remarkably good linear shape, which indicates that $C(T)$ is essentially made of linear and cubic terms. Furthermore, there is no clear indication of a hyperfine term ($C \propto T^{-2}$) in the $C(T)$ curve. Such a term, related to Zeeman splitting of the Mn and Pr nuclear levels, has a

TABLE I. Best parameters obtained from the fitting of the curves in Fig. 4 by Eq. (2) or Eq. (3) (see text). The associated units are γ (10^{-3} J K^{-2} mol^{-1}), β_3 (10^{-4} J K^{-4} mol^{-1}), β_5 (10^{-7} J K^{-6} mol^{-1}), δ (10^{-2} J K^{-2} mol^{-1}), and Δ (K).

Compound	State	γ	β_3	β_5	δ	Δ
PrCa50	[ZFC-0T]	9.84	2.57	1.76	-	-
PrCa50Ga5%	[ZFC-9T]	8.30	1.81	4.44	-	-
PrCa50Ga5%	[REM-0T]	8.30	1.89	5.78	-	-
PrCa50Ga5%	[ZFC-0T]	8.30	1.89	5.76	6.32	4.06
PrCa50Ga5%	[ZFC-0T]	0	1.89	6.76	6.66	3.01
PrCa50Ga5%	[ZFC-0T]	8.30	2.57	2.64	5.63	3.79
PrCa50Ga5%	[ZFC-0T]	0	2.57	3.47	6.06	2.77

moderate influence when T is not too low. Instead of including in the fitting procedure this contribution whose influence is weak and whose determination would be unreliable in our case (since $T > 2.2$ K), we preferred to deliberately neglect it. We made the same approximation for all curves of Fig. 4. Accounting for the slight upward curvature of [ZFC-0T] in PrCa50, a T^5 term (standard correction to the cubic term to account for the lattice contribution) was also included in the fitting expression, leading to

$$C = \gamma T + \beta_3 T^3 + \beta_5 T^5. \qquad (2)$$

The best parameters found for [ZFC-0T] of PrCa50 are given in Table I. The β_3 value is a little bit larger than expected for the lattice contribution in perovskite manganites. Indeed, using the relation $\theta_D = (12\pi^4 pR / 5\beta_3)^{1/3}$, where R is the gas constant and p the number of atoms per molecule, one finds a Debye temperature equal to 335 K, whereas the usual values in manganites rather lie in the range 350–450 K. Actually, a part of the β_3 value might originate from spin-wave excitations in the AF order.[10,11,23–25] While there are not yet theoretical predictions in the case of CE-type AF ordering, it is well established that spin waves yield a T^3 contribution in the more standard G-type AF. Since PrCa50 is strongly insulating, the γT term can hardly be related to a standard free-carrier contribution. Actually, such a linear term was often found in insulating manganites, and it was generally attributed to some disordering effects affecting the spin, charge, or orbital degrees of freedom. The γ value we found is consistent with those previously reported in insulating manganites.[14,23,24]

B. $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$: F state under 9 T and 0 T

Let us now tackle the case of (PrCa50)Ga5%, for which one is facing two very different states: [ZFC-0T] corresponds to a weak AFCOO state with effects of disorder leading to spin-glass-like features, whereas [REM-0T] and [ZFC-9T] correspond to a bulk F state. Instead of fitting independently each of these curves with a lot of free parameters, we propose to analyze the whole set of data in a consistent way, following a step-by-step approach.

Let us start with [ZFC-9T], which has a well-known magnetoelectronic state (ferromagnetic, conducting). In addition,

one can assume that the spin-wave contribution is essentially quenched under 9 T.[20] Thus, consistently with the slight upward curvature seen in Fig. 4, the [ZFC-9T] curve was just fitted by Eq. (2). The derived parameters are given in Table I. Since [ZFC-9T] is a conducting state, the linear term could be ascribed to an electronic contribution, though one obtains a γ value very close to that of PrCa50. This is a striking coincidence since the two states are totally different, one being ferromagnetic, conducting and the other insulating, antiferromagnetic. This result emphasizes the questionable origin of some linear terms in manganites.[11] In other respects, β_3 in [ZFC-9T] is smaller than in PrCa50, which is consistent with the implication of AF spin waves in the latter case. Actually, β_3 in [ZFC-9T] has a value expected for the lattice contribution in manganites ($\theta_D \simeq 375$ K).

The curve of [REM-0T] is very close to that of [ZFC-9T], consistently with the fact that they correspond to the same ferromagnetic state. At first glance, the slightly higher location of [REM-0T] could be ascribed to the development of the ferromagnetic spin-wave contribution, a term impeded by the large field in [ZFC-9T]. Nevertheless, the difference between these two curves does not display a $T^{3/2}$ dependence (typical of ferromagnetic spin waves), but rather a cubic one. It has also been checked out that the inclusion of a $T^{3/2}$ term, beside or instead of the linear term, did not improve the fitting quality in the case of [REM-0T]. Thus the curve of [REM-0T] was just fitted by the same expression as used for [ZFC-9T], yielding the γ, β_3, and β_5 parameters gathered in Table I.

C. $Pr_{0.5}Ca_{0.5}Mn_{0.95}Ga_{0.05}O_3$: Disordered AFCOO state under 0 T

The [ZFC-0T] curve exhibits a pronounced downward curvature, reminiscent of previously reported results in strongly AFCOO compounds.[23,25,26] Nevertheless, it seems difficult to ascribe this special shape to a characteristic contribution of COO since it is not observed in the much-better-established, long-range COO of PrCa50 (see Fig. 4). Let us also note that the [ZFC-0T] curve of (PrCa50)Ga5% cannot be accounted for by any combination of the PrCa50 [ZFC-0T] curve (AFCOO state) and (PrCa50)Ga5% [REM-0T] curve (F state). Actually, there is rather a specific term related to disorder in the [ZFC-0T] curve of (PrCa50)Ga5%, a feature that can be well consistent with the prominent glassy behavior displayed in $\chi_{dc}(T)$ (inset of Fig. 1).

In the simplest cases, a spin-glass-like behavior is reflected by a linear term in $C(T)$,[13] which is clearly not the case here. Deviations from this simple law, however, were often observed even in canonical spin glasses. For instance, linear extrapolations of C/T-vs-T^2 plots were found to yield negative ordinates,[27] a behavior that can be accounted for by attributing a $\delta T \exp(-\Delta/T)$ law to the spin-glass contribution. Such a phenomenological expression leads to downward curvature as that displayed by [REM-0T].[28] Furthermore, one has to face the question to know whether a simple linear term—as found in the previous states of Fig. 4—must also be included in the case of [ZFC-0T]. Since the occurrence of this term seems to be quite independent of the mag-

netoelectronic state (see Table I), such a possibility cannot be ruled out. Finally, the fitting of the [ZFC-0T] curve was thus carried out by the following expression:

$$C = \gamma T + \beta_3 T^3 + \beta_5 T^5 + \delta T \exp(-\Delta/T). \quad (3)$$

It is obviously difficult to get reliable values with so many free parameters. Actually, the analysis of the other curves in Fig. 4 can allow us to put some reasonable constraints on two of these parameters: first, we considered that the β_3 value should be in between that found for [REM-0T], which is representative of the lattice contribution only, and that of PrCa50, which includes an additional contribution from AF spin waves; second, we considered that γ should lie in between 0 and the value found in the other states (8.3 mJ K^{-2} mol^{-1}). This gives rise to four different sets of fixed parameters, leading to different β, δ, and Δ values (see Table I) when fitting [ZFC-0T] with Eq. (3). One can notice that the free parameters get rather close values in all cases.

D. "Excess term" in the specific heat of AFCOO manganites

In previous studies, the existence of a large specific heat at low T with a downward curvature in a C/T-vs-T^2 plot was claimed to be an intrinsic property of the charge and orbital ordering.[23,25,26] Our observation of such features in a weak, disordered COO, and not in the strong, pure COO (PrCa50), puts in doubt this idea. In a previous study, the COO origin of the anomalous specific heat was supported by a comparison between PrCa50 and (PrCa50)Cr3%, which showed a lower location of the $C(T)$ with no more downward curvature in the latter case.[23] It must be realized, however, that Cr is very efficient to destroy COO and that 3% is enough to induce a large ferromagnetic component.[5,29,30] The [ZFC-0T] curve of (PrCa50)Cr3% in Ref. 23 appears to be very close to our [REM-0T] curve in (PrCa50)Ga5%, in agreement with the ferromagnetic nature of both states. Actually, our investigation of the [ZFC-0T] state in (PrCa50)Ga5% demonstrates that when AFCOO is just destabilized without being destroyed, the specific heat *increases* and the downward curvature *appears*. We thus conclude that the excess specific heat showing a downward curvature (in C/T vs T^2) is not intrinsically related to AFCOO, but rather to the introduction of disorder in AFCOO.

VII. CONCLUSION

In conclusion, this study shows that slight substitutions on the Mn sublattice in a strongly AFCOO compound totally modify the magnetoelectronic ground state. The setting up of COO and AF (CE type) at high T is no longer reflected in the specific-heat curve. The remaining AFCOO becomes short range and coexists with a disordered magnetic phase displaying spin-glass-like features. Application of high enough magnetic field at low T can switch such a compound to a bulk ferromagnetic state. The intrinsic Curie temperature of this field-induced ferromagnetism is close to 40 K under zero field, and it increases up to about 110 K under 9 T, without substantial broadening of the transition. The first-order char-

acter of the temperature-induced transition under 9 T, from ferromagnetic to a weak AFCOO state, is supported by a close connection between specific heat and magnetization, obeying the Clausius-Clapeyron relationship.

All encountered magnetoelectronic states were investigated by analyzing the temperature dependence of specific heat in the very-low-T regime. Surprisingly, the $C(T)$ curves of the substituted sample in the ferromagnetic state are rather close to that of the unsubstituted compound, while their mag-

netoelectronic states are very contrasted. In the disordered AFCOO state of the substituted compound, the specific heat is much larger than in the other cases, with a very different temperature dependence. The whole set of results suggests that this extra specific heat is actually related to the disordered character of the AFCOO rather than to the AFCOO itself. Investigations of Mn-site substitutions in manganites displaying various magnetoelectronic ground states deserve to be carried out to go further into this issue.

[1] For a review, see *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides*, edited by C. N. R. Rao and B. Raveau (World Scientific, Singapore, 1998); *Colossal Magnetoresistance Oxides*, edited by Y. Tokura (Gordon and Breach, London, 1999).

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