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# Ga and Ba substitution in charge ordered $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ : exceptional predisposition of the $x = 0.43$ compound to ferromagnetism

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## Abstract

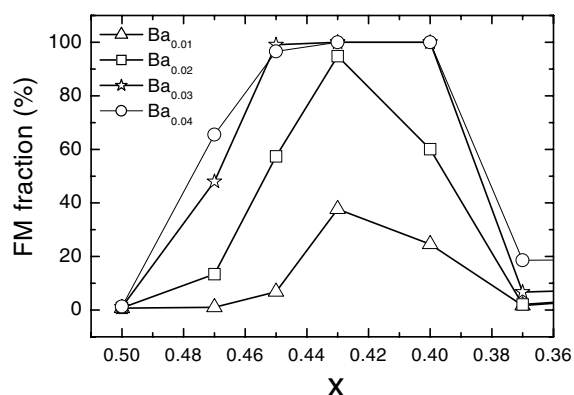
The effect of low substitution levels of Ga for Mn and of Ba for Ca upon the magnetic properties of orbital–charge ordered manganites has been studied for  $0.33 < x \leq 0.50$  in  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ . It is shown that, for very small Ga or Ba contents ( $\sim 2\%$ ), a ferromagnetic ground state can be created. More importantly, the ferromagnetic fraction, very small for  $x \approx 0.37$ – $0.33$  and  $x = 0.50$ , goes abruptly through a maximum for the  $x \approx 0.43$  compound, which can be considered as a full ferromagnet at 2.5 K, with ferromagnetic fractions of 95–100% for 2–3% Ba. The role of the local ‘counter-distortion’ introduced by Ga or Ba in the appearance of ferromagnetism is discussed in the context of orbital–charge ordering and phase separation.

## 1. Introduction

The numerous studies of perovskite manganites have shown the important role of orbital–charge ordering and phase separation in the magnetic and transport properties of these oxides. This is indeed the case for the antiferromagnetic insulators  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ , which for  $x = 0.50$  were found to be orbital–charge ordered (OO–CO), in the form of 1:1 alternating  $\text{Mn}^{3+}/\text{Mn}^{4+}$  stripes [1–3]. It was then demonstrated that the OO–CO state can be melted into a ferromagnetic metallic (FM) state by various stimuli such as a magnetic field [2], x-ray irradiation [4], pulsed laser illumination [5], current injection [6], or by replacing Mn with small amounts of magnetic cations [7, 8].

The magnetic phase diagram of the system  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  [9] shows that the 1:1 OO–CO state persists over the whole range  $0.33 \leq x \leq 0.50$ , but is progressively destabilized as  $x$  decreases. The continuous decrease of the stability of the OO–CO state versus  $x$  is demonstrated by the progressive decrease of the critical magnetic field for the OO–CO to FM

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**Figure 1.** The ferromagnetic fraction at 2.5 K for the barium substituted manganites  $\text{Pr}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$ . The  $\delta$  values for the Ba content are shown as labels in the figure.

state transition from about 27 T for  $x = 0.50$ , to 8 T for  $x = 0.40$ , to only 4 T for  $x = 0.30$  [2]. Nevertheless, the thermopower studies carried out by Yamada *et al* [10] for  $x \sim 0.35$  and the evidence for a charge gap in the optical absorption for the polarization at  $x \sim 0.40$  described by Okitomo *et al* [11] suggest that the magnetic properties in this domain should not vary so continuously versus  $x$ . This viewpoint is reinforced by the recent discovery of a new kind of OO–CO ordering for  $x = 3/8$  by Asaka *et al* [12].

Bearing in mind the latter results, we have revisited the system  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ , studying the influence of the substitution of very small amounts of barium for calcium and of gallium for manganese versus  $x$  upon the magnetic properties of these oxides for the orbital–charge ordered (OO–CO) domain  $0.33 \leq x \leq 0.50$ . We confirm the existence of ultrasharp magnetization steps at 2.5 K in the whole domain, as previously described for  $x = 0.50$  and 0.40 [13–17]. But more importantly, we show that the Ba substituted  $\text{Pr}_{0.57}\text{Ca}_{0.43}\text{MnO}_3$  phase exhibits an exceptional ferromagnetic (FM) fraction up to 95–100% for very low Ba levels (2–3%). We demonstrate that whatever the dopant, Ba or Ga, for a given substitution level, the FM fraction exhibits a bell shaped curve versus  $x$ , centred on  $x \sim 0.43$ , the values for  $x$  close to 0.50 and to 0.37–0.33 remaining very small. We suggest that this evolution is closely related to the ‘counter-distortion’ introduced by Ba or Ga in the antiferromagnetic matrix.

## 2. Experimental section

Polycrystalline samples of  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ ,  $\text{Pr}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  and  $\text{Pr}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Ga}_{0.02}\text{O}_3$  were prepared by conventional solid state reaction according to the experimental procedure previously reported [13–16]. The chemical and structural quality of the samples was tested by electron diffraction (ED) and energy dispersive analysis (EDS). The zero-field cooling  $M(T)$  curve was measured with a vibrating sample magnetometer in a magnetic field of 1.45 T. The  $M(H)$  measurements at 2.5 K were performed with two types of extraction magnetometer (SQUID detection for fields up to 5 or 5.5 T and without a SQUID up to 9 T). The  $M(H)$  data were collected 30 s after the magnetic field stabilization by varying the magnetic field in steps of 0.25 T. In order to quantify the FM fraction in different samples, their  $M$  data, measured in a moderate magnetic field (0.25 T) at 2.5 K, were normalized by the value obtained in similar conditions for the related bulk ferromagnet  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.95}\text{Ru}_{0.05}\text{O}_3$  [13].

## 3. Results and discussion

The evolution of the induced ferromagnetic fraction FM (%) versus  $x$  in a weak magnetic field of 0.25 T measured at 2.5 K for the barium-doped manganites  $\text{Pr}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  (figure 1)

**Table 1.** The FM fraction (%) for  $\text{Pr}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  and  $\text{Pr}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Ga}_{0.02}\text{O}_3$ .

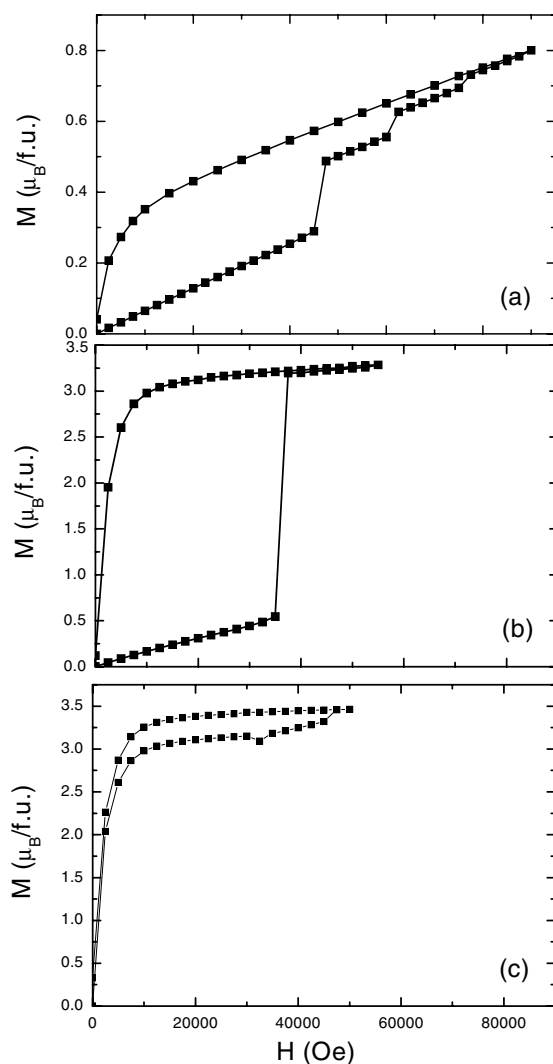
$\delta$	$x = 0.5$	$x = 0.47$	$x = 0.45$	$x = 0.43$	$x = 0.4$	$x = 0.37$
0		0.9	0.9	1.4	1.3	1.5
0.01	0.8	1	13	38	25	1.7
0.02	0.8	13	57	95	60	2
0.03	0.9	48	99	100	100	7
0.04	1.3	66	97	100	100	19
0.05	1.5					64
0.06	1.4					100
Ga <sub>0.02</sub>	1.2	23	39	61	43	3

shows that, starting from  $x = 0.50$  for a given Ba content, the FM fraction first increases rapidly as  $x$  decreases, reaches a maximum around  $x \sim 0.43$  and decreases down to  $x = 0.37$ . For low Ba contents ( $\delta = 0.01$ – $0.02$ ) this evolution appears as a peak at  $x = 0.43$ , whereas the FM fraction reaches 100% for several compositions around  $x = 0.43$  for higher Ba contents ( $\delta = 0.03$ – $0.04$ ). More importantly the following features must be emphasized:

- (i) The FM fraction is very small for  $x = 1/2$ , and practically not modified by the Ba doping, remaining fixed at about 1%, whatever the Ba content (1–4%).
- (ii) The FM fraction is also small for  $x = 0.37$  (3/8), though it increases more significantly with the Ba content up to 19% for  $\delta = 0.04$  (table 1).
- (iii) In contrast, for  $x = 0.43$ , the Ba substitution induces a considerable FM fraction which already reaches 95% for only 2% Ba and 100% for 3% Ba (table 1).
- (iv) For a given  $x$  value, the FM fraction increases with the barium content. This effect is dramatic for  $x = 0.43$  and decreases rapidly as  $x$  deviates from this value, on both sides, towards  $x = 0.50$  and  $0.37$ .

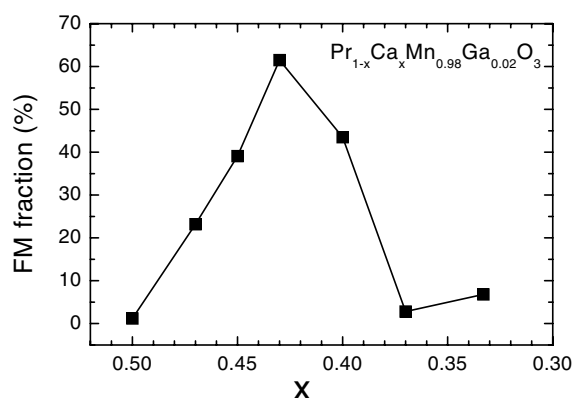
Bearing in mind that the magnetic field is one of the stimuli which can melt the OO–CO state into a FM state, we compare herein the  $M(H)$  curves registered at 2.5 K for the series  $\text{Pr}_{1-x}\text{Ca}_{x-0.02}\text{Ba}_{0.02}\text{MnO}_3$  (figure 2) with  $x = 0.50, 0.43$  and  $0.37$ . For  $x = 0.50$  one observes that the saturation is far from being achieved (figure 2(a)): a maximum magnetization of only  $0.8 \mu_B$  is reached up to 9 T, three steps being necessary to reach this low value. The sample with  $x = 0.37$ , although it also exhibits a very small FM fraction ( $\sim 2\%$ ), is much more sensitive to the magnetic field; one indeed observes (figure 2(b)) a behaviour similar to that of the  $x = 0.50$  sample up to about 3.5 T, where a magnetization of  $\sim 0.5 \mu_B$  is obtained, but beyond this field an ultrasharp step is observed leading to a magnetization value of  $3.2 \mu_B$ , i.e. close to the saturation. In contrast to the two other samples, the  $x = 0.43$  sample can be considered as a practically pure ferromagnet (figure 2(c)), no step being necessary to reach a high value of the magnetization, close to the saturation ( $3.5 \mu_B/\text{fu}$ ). These results show that for this 2% Ba-doped sample the critical field necessary to induce full ferromagnetism is much higher for the  $x = 0.50$  sample ( $>9$  T) than for the  $x = 0.37$  sample ( $\sim 3.5$  T), but decreases as  $x$  deviates from these two values, tending towards  $\sim 0$  T for  $x = 0.43$ . This kind of evolution of the induced ferromagnetism can be generalized to various Ba contents as shown in table 2. One observes that the maximum magnetization  $M_{\text{max}}$  reaches saturation more rapidly for  $x = 0.43$  (2% Ba) than for  $x = 0.37$  (3% Ba) and than for  $x = 1/2$  ( $>6\%$  Ba).

The substitution of a non-magnetic cation for manganese in  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  also induces ferromagnetism in the absence of a magnetic field. This is illustrated by the evolution of the FM fraction versus  $x$  for  $\text{Pr}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Ga}_{0.02}\text{O}_3$  (figure 3). Remarkably, one observes that for this Ga content the FM fraction goes through a maximum value for  $x = 0.43$ ,



**Figure 2.** The magnetic field ( $H$ ) dependence of the magnetization ( $M$ ) at 2.5 K for  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_{0.02}\text{MnO}_3$ : (a)  $x = 0.50$ ; (b)  $x = 0.37$ ; (c)  $x = 0.43$ .

whereas the  $x = 0.50$  and  $0.37$  samples are practically not sensitive to the substitution (FM  $\sim 1\text{--}8\%$ ), similarly to the Ba effect. Nevertheless, Ga is less efficient than Ba for inducing full ferromagnetism: a maximum FM fraction of 61% is only reached in the case of Ga, compared to 95% for the same Ba content of 2% for  $x = 0.43$ . In fact the situation is a little more complex: close to the OO–CO phase with  $x = 0.50$ , i.e.  $0.47 \leq x \leq 0.50$ , Ga induces a slightly higher FM fraction than Ba, whereas for  $0.37 \leq x \leq 0.43$ , the opposite is observed, i.e. Ga induces a much smaller FM fraction than Ba (see table 1 and compare figures 1 and 3). The effect of the magnetic field on these Ga-doped manganites follows the same evolution versus  $x$ , as shown by the  $M(H)$  curves (figure 4). The  $x = 1/2$  Ga-doped manganite  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.98}\text{Ga}_{0.02}\text{O}_3$  (figure 4(a)), like the Ba-doped phase (figure 2(a)), does not reach saturation, but exhibits a higher maximum magnetization ( $\sim 1.5 \mu_{\text{B}}/\text{f.u.}$  in 5 T to be compared to  $0.8 \mu_{\text{B}}/\text{f.u.}$  in 9 T for the Ba-doped phase) and smaller ‘critical’ fields (2.8 and 5.3 T against 4.5 and 6 T for the Ba-doped phase). The  $x = 0.37$  sample (figure 4(b)), like the Ba-doped phase (figure 2(b)), exhibits one magnetization step at about 3.5 T, but the



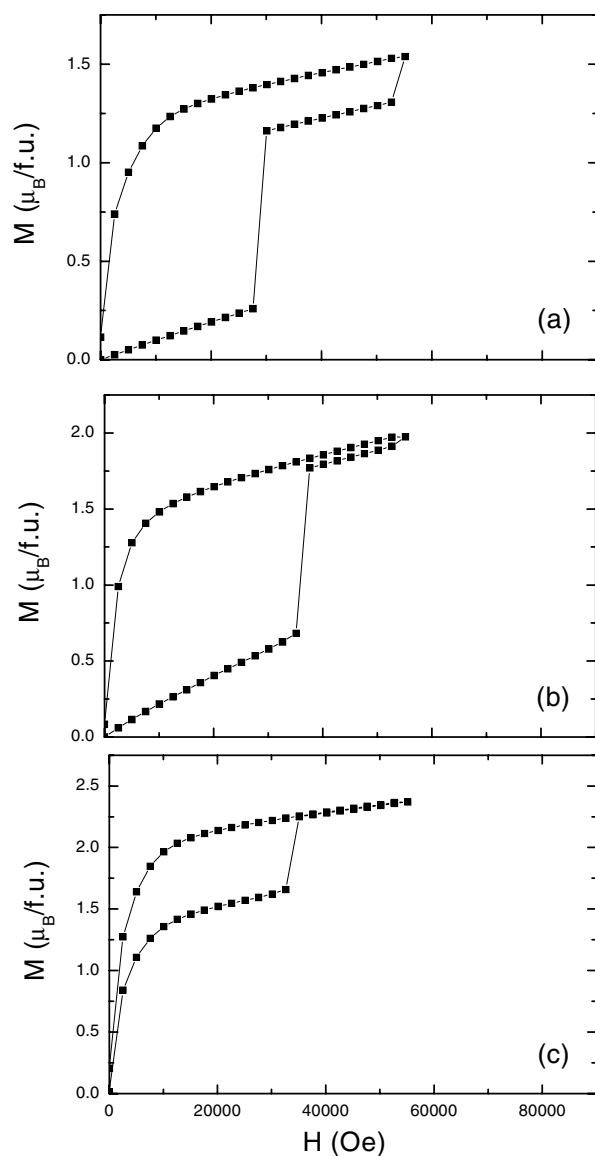
**Figure 3.** The ferromagnetic fraction as a function of  $x$  for the Ga substituted manganites  $\text{Pr}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Ga}_{0.02}\text{O}_3$ .

**Table 2.** The maximum magnetization  $M_{\text{max}}$  in either 5 or 5.5 or 9 T ( $=H_{\text{max}}$ ) and the number of steps (including the position of the steps) measured at 2.5 K for  $\text{Pr}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  with  $x = 0.5, 0.43$  and  $0.37$ .

$x$		1% Ba	2% Ba	3% Ba	4% Ba	5% Ba	5% Ba
0.5	$M_{\text{max}}$ ( $\mu_{\text{B}}/\text{fu}$ )	0.6	0.8	1.6	2.9	2.7	3.3
	Number of steps	1 (4.5 T)	3 (4.5, 6.0, 7.5 T)	3 (3.3, 4.5, 7.0 T)	2 (3.5, 4.8 T)	1 (4.0 T)	1 (4.8 T)
	$H_{\text{max}}$ (T)	5.5	9	9	5.5	5	5.5
0.43	$M_{\text{max}}$ ( $\mu_{\text{B}}/\text{fu}$ )	2.6	3.5	3.7	3.7		
	Number of steps	1 (3.3 T)	0	0	0		
	$H_{\text{max}}$ (T)	5.5	5	5.5	5.5		
0.37	$M_{\text{max}}$ ( $\mu_{\text{B}}/\text{fu}$ )	2.2	3.3	3.8	3.6	3.8	3.7
	Number of steps	1 (4.0 T)	1 (3.5 T)	2 (3.0, 5.3 T)	1 (2.5 T)	1 (2.8 T)	0
	$H_{\text{max}}$ (T)	5.5	5.5	5.5	5.5	5.5	5.5

maximum magnetization ( $\sim 2 \mu_{\text{B}}/\text{fu}$ ) does not reach saturation unlike the latter ( $\sim 3.5 \mu_{\text{B}}/\text{fu}$ ). The  $x = 0.43$  sample (figure 4(c)) exhibits the highest maximum magnetization of the series ( $M_{\text{max}} = 2.4 \mu_{\text{B}}/\text{fu}$ ) in 5.5 T, but in contrast to the Ba-doped phase (figure 2(c)) does not reach saturation ( $\sim 3.5 \mu_{\text{B}}/\text{fu}$ ); moreover it exhibits one magnetization step at about 3 T, whereas no step is required to reach saturation in the Ba-doped phase.

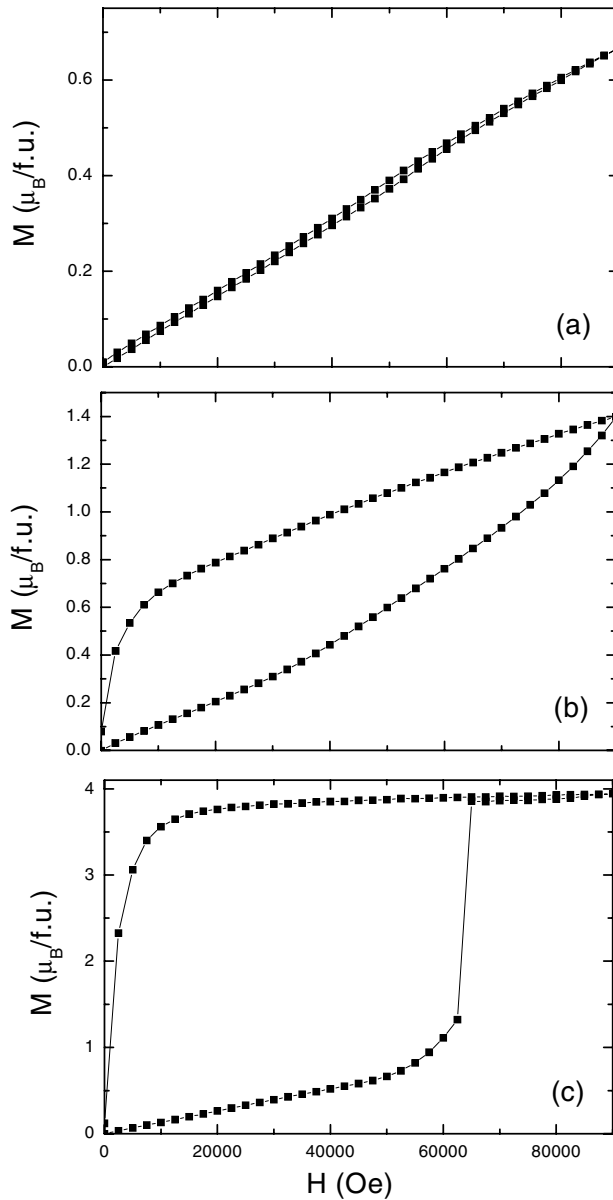
At this point of the investigation, it is necessary to compare the doped manganites and the pristine ones, prepared in the same conditions. The evolution of the FM fraction of the latter (table 1) is very different: one does not observe any maximum of FM around  $x \sim 0.43$ , in contrast to the doped samples case, and the FM values remain small, ranging from 0.9% to 1.5%. The  $M(H)$  curves of the pristine phases  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  registered at 2.5 K (figure 5) indeed show that, in contrast to the Ba- and Ga-doped phase cases, no complete melting of the OO-CO state can be obtained by the application of a 9 T field in the  $x = 0.43$  sample. For the  $x = 0.50$  sample (figure 5(a)), the increasing and decreasing branches of the  $M(H)$  curve are superimposed without any hysteresis and the maximum magnetization value is only  $\sim 0.7 \mu_{\text{B}}/\text{fu}$  in 9 T. This indicates that for  $x = 0.50$  charge ordering is very robust and that 9 T is not sufficient to totally melt it. For  $x = 0.43$ , the  $M(H)$  curve (figure 5(b)) shows a hysteresis, as well as a larger magnetization ( $\sim 1.4 \mu_{\text{B}}$ ), but a field of 9 T is still not sufficient to melt the OO-CO state into a FM one, in contrast to the doped sample cases. Finally, for  $x = 0.37$  (figure 5(c)) saturation of the magnetization can be reached, with one step, showing a critical field of 6.3 T. This decrease of the critical magnetic field with  $x$  is in agreement with previous



**Figure 4.** Isothermal ( $T = 2.5$  K)  $M(H)$  curves for three  $\text{Pr}_{1-x}\text{Ca}_x\text{Mn}_{0.98}\text{Ga}_{0.02}\text{O}_3$  samples: (a)  $x = 0.50$ ; (b)  $x = 0.37$ ; (c)  $x = 0.43$ .

observations [2] and does not support any eventual effect of the additional charge ordering reported for  $x = 3/8$  [9]. The systematic electron microscopy study of different samples, and especially of the  $x = 0.37$  (i.e.  $3/8$ ) sample, versus temperature, from room temperature down to 90 K, confirms the 1:1 OO–CO state but indeed shows that this second type of orbital–charge ordering does not exist in our samples. Similarly, the systematic investigation of 2% Ba (or Ga) substituted samples, by means of electron diffraction, versus temperature did not evidence any additional orbital charge ordering, beside the classical 1:1 OO–CO state.

In fact, the evolution of ferromagnetism in these Ba- or Ga-doped manganites can be partly explained on the basis of the coexistence of structural and electronic phase separation. The introduction of barium in the distorted perovskite cages or of gallium in the Jahn–Teller (JT) distorted octahedral  $\text{Mn}^{3+}$  sites locally hinders the distortion of the structure within the



**Figure 5.**  $M(H)_{2.5 \text{ K}}$  curves for the three pristine  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  samples: (a)  $x = 0.50$ ; (b)  $x = 0.43$ ; (c)  $x = 0.37$ .

distorted antiferromagnetic matrix. This local structural phase separation is then at the origin of the electronic phase separation, favouring the formation of FM metallic regions in the insulating AFM matrix.

In order to explain the effect of chemical doping with barium or gallium versus  $x$ , two antagonist effects upon the ferromagnetism must be taken into consideration. The first one concerns the stability of charge ordering, called the CO effect, which decreases as the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio increases, as observed from the magnetic field effect [2]. The second effect is the local increase of the symmetry of the structure induced by chemical doping either with barium or with gallium, called the ‘counter-distortion’ effect since it counterbalances the Jahn–Teller distortion of the  $\text{Mn}^{3+}$  octahedra surrounding  $\text{Ba}^{2+}$  or  $\text{Ga}^{2+}$ . This local ‘counter-



distortion' becomes more efficient as the number of JT  $\text{Mn}^{3+}$  octahedra surrounding each Ba or Ga species becomes smaller. Like charge ordering, the geometrical counter-distortion effect decreases as  $x$  increases (i.e. as the  $\text{Mn}^{3+}$  content increases). Thus for  $x = 0.50$  the counter-distortion effect is the strongest and locally favours the FM state, but unfortunately CO is extremely stable and compensates or overcomes the counter-distortion effect so that FM does not grow for low Ba or Ga contents. For  $x = 0.37\text{--}0.33$  ( $\text{Mn}^{3+}/\text{Mn}^{4+} = 1.7\text{--}2$ ), the CO state is much less stable but unfortunately the counter-distortion effect has decreased dramatically due to the too large number of distorted  $\text{Mn}^{3+}$  octahedra locally surrounding each Ba or Ga impurity. As a consequence, the counter-distortion is not sufficient to overcome the CO effect and the FM does not grow either. In contrast, as  $x$  deviates from  $x = 0.50$  the stability of CO decreases in a first step abruptly, as shown by the magnetic field effect [2], whereas the counter-distortion decreases but is most probably much less affected, so the counter-distortion prevails over charge ordering as  $x$  decreases down to  $x = 0.43$ . Consequently the FM fraction increases and is maximum for this particular composition. Beyond  $x = 0.43$ , the counter-distortion continues to decrease because of the increasing number of  $\text{Mn}^{3+}$  octahedra around each Ba or Ga species, and the CO stability decreases but more smoothly (see [2]) so the FM fraction decreases with  $x$  down to  $x = 0.37$ . Thus for the two limits  $x = 0.50$  and  $0.33\text{--}0.37$ , the charge ordering effect prevails over the counter-distortion, whereas about halfway between these two compositions, at  $x \approx 0.43$ , the counter-distortion prevails strongly over the charge ordering, so a maximum ferromagnetic fraction is induced by Ba or Ga doping. Note that the Ga-doped samples always exhibit a smaller FM fraction than the Ba-doped ones. This is easily explained by the fact that the introduction of non-magnetic impurity on a Mn site tends to break the ferromagnetic interactions.

#### 4. Conclusion

We have shown that the introduction of small amounts of Ba or Ga on the A or Mn sites ( $\sim 2\%$ ) induces high ferromagnetic fractions in the CE or pseudo-CE type  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  manganites even at low magnetic fields ( $\sim 0.25$  T). More importantly we demonstrate that this effect goes through a maximum for  $x \sim 0.43$ , for which a ferromagnetic ground state can be created by barium doping, whereas the limits  $x = 0.50$  and  $0.37\text{--}0.33$  remain little affected. This evolution can be explained by the antagonist effects of the stability of charge ordering and the local geometric 'counter-distortion' which is induced around each species (Ba or Ga) by chemical doping.

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