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# Influence of Ba substitution upon ferromagnetism in charge ordered $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ : singular behaviour of $x = 0.43$

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## Abstract

The study of the substitution of Ba for Ca in the orbital-charge ordered manganites  $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$ , with  $0.37 \leq x \leq 0.50$ , for low Ba levels (smaller than 6%) shows that, similarly to the  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  system (Zhu *et al* 2004 *J. Phys.: Condens. Matter* **16** 2861), a ferromagnetic ground state is obtained. The evolution of the ferromagnetic fraction in zero field is quite similar: it goes through a maximum at  $x = 0.43$ , which, for 4% Ba, is like for Pr a full ferromagnet at 2.5 K, with a ferromagnetic fraction of 90%. The higher Ba level necessary to reach the FM state in Nd phases compared to Pr is explained in terms of the antagonist effects of charge-orbital stability and local counter-distortion due to Ba. The different behaviour in a magnetic field, and especially the much larger magnetizations reached by Nd phases with respect to the Pr ones,  $0.43 < x \leq 0.50$ , is explained in terms of Nd–Mn magnetic interactions, which destabilize the CE-type AFM structure.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The possibility to induce ferromagnetism in orbital-charge ordered (OO–CO) manganites  $\text{Ln}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $\text{Ln} = \text{Pr}$  to  $\text{Lu}$ ) is a very important issue, since it is at the origin of the appearance of colossal magnetoresistance (CMR) in these materials. The various studies of these OO–CO manganites, with  $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}$  [1–5], have shown that the orbital-charge ordering appears in the form of alternating  $\text{Mn}^{3+}/\text{Mn}^{4+}$  stripes and that the corresponding insulating state exhibits a CE-type antiferromagnetic structure. For  $\text{Ln} = \text{Pr}$  it was shown that the OO–CO state can be melted by application of a magnetic field, leading to a ferromagnetic metallic state [3]. Nevertheless the latter authors demonstrated that the required magnetic field to induce such a transition is high for  $x = 0.50$ , i.e.  $\sim 27$  T, and decreases down to 4 T as  $x$  decreases to 0.40. Moreover, the high magnetic field investigations of the manganites

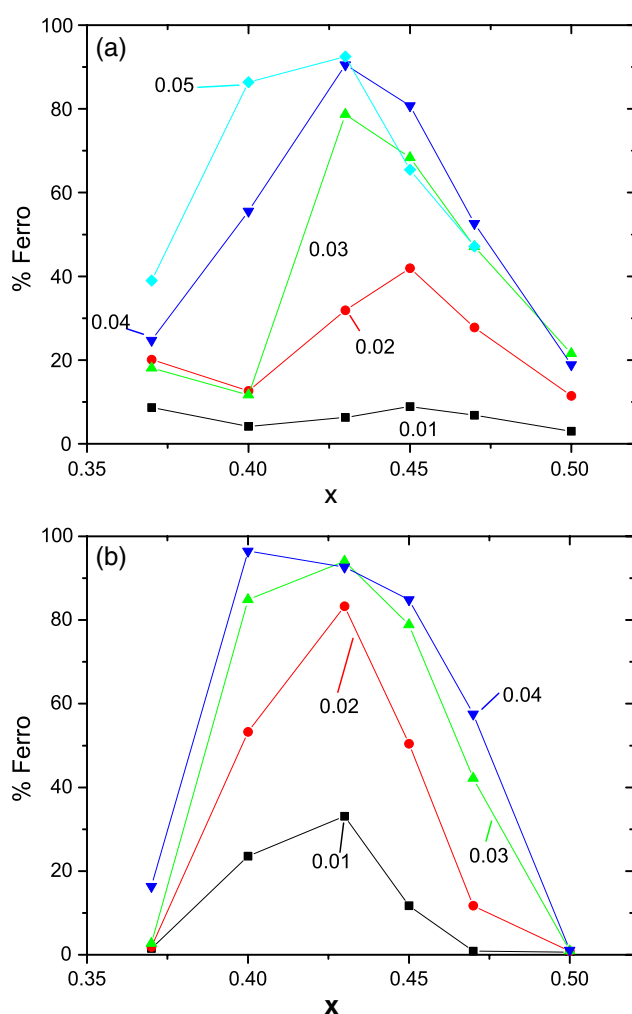
$\text{Ln}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$  [6, 7] have shown that the critical field that characterizes the stability of the OO–CO state increases dramatically as the size of the  $\text{Ln}^{3+}$  cation decreases, except for neodymium, which exhibits a critical field, slightly smaller than that of praseodymium, in spite of its smaller size.

Another way to induce ferromagnetism in the OO–CO manganites consists in using chemical doping either on the A or on the Mn sites. Low substitution levels of magnetic cations such as Cr or Ru for Mn in  $\text{Ln}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  [8, 9] allow ferromagnetic ground states to be induced even in the absence of magnetic field, via phase separation phenomena [10]. The substitution of non-magnetic cations, such as Ga for Mn or Ba for Ca, can lower the critical magnetic field significantly in  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ , leading to ultrasharp magnetization multisteps [11]. More importantly, we demonstrated that for  $x < 0.50$  in the series  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ferromagnetism can be induced by Ga or Ba doping, even in the absence of magnetic field, and that a full ferromagnet could be obtained for  $x = 0.43$ , at 2.5 K [12].

Bearing in mind the exceptional behaviour of the doped  $\text{Pr}_{0.57}\text{Ca}_{0.43}\text{MnO}_3$  manganite and the rather close critical fields of  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  and  $\text{Nd}_{0.50}\text{Ca}_{0.50}\text{MnO}_3$ , we have explored the series  $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$  doped with barium. In this paper, we show that the Ba-doped  $\text{Nd}_{0.57}\text{Ca}_{0.43}\text{MnO}_3$  manganite also exhibits an exceptional predisposition to ferromagnetism. We also evidence that the Ba-doped  $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$  phases reach much larger magnetization under field than the Pr-ones for  $0.43 < x \leq 0.50$  and that the reverse is obtained for  $0.37 \leq x < 0.43$ . We discuss the differences between Nd and Pr on the basis of the additional field induced moments on the Nd sites.

## 2. Experimental section

Polycrystalline samples  $\text{Nd}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  were prepared by conventional solid state reaction, using the same experimental procedure as for  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  [11]. The cationic composition and structural nature of the samples were checked by energy dispersive analysis (EDS) coupled with electron diffraction (ED). The magnetization versus  $T$  and versus  $H$  at 2.5 K were carried out with two types of extraction magnetometers (SQUID up to 5.5 T and without SQUID up to 9 T). The  $M(H)$  data were collected 30 s after the installation of the magnetic field which is varied by steps of 0.25 T. The quantification of the ferromagnetic fraction was made by first estimating the expected maximum values of the saturation magnetization ( $M_S$ ) for Pr- and Nd-based manganites [3, 13]. For these manganites,  $\text{Pr}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  and  $\text{Nd}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$ , the maximum  $M_S$  values correspond to  $3.9 \mu_B$  and  $4.4 \mu_B$ , respectively. Second, from the  $M_S$  values obtained for the present series, reaching maximum values of  $4.0 \mu_B$  and  $4.3 \mu_B$  for  $\text{Pr}_{0.6}\text{Ca}_{0.33}\text{Ba}_{0.07}\text{MnO}_3$  and  $\text{Nd}_{0.6}\text{Ca}_{0.33}\text{Ba}_{0.07}\text{MnO}_3$  respectively, it turns out that these samples are near 100% ferromagnetic. Then, in order to estimate the ferromagnetic fraction in all the samples, it is important to use a small magnetic field value to favour the FM alignment of domains without influencing the CO/OO to FM transition [14]. We have thus used the magnetization values ( $M$ ) of the  $M(H)$  curves for the smallest magnetic field values (0.25 T) for the  $\approx 100\%$  ferromagnetic compound,  $2.45 \mu_B$  and  $2.55 \mu_B$  for  $\text{Pr}_{0.6}\text{Ca}_{0.33}\text{Ba}_{0.07}\text{MnO}_3$  and  $\text{Nd}_{0.6}\text{Ca}_{0.33}\text{Ba}_{0.07}\text{MnO}_3$ , respectively. The FM fractions given in the following are estimated by dividing the  $M(H = 0.25 \text{ T})$  value by the values of these reference samples. It must be pointed out that this determination is valid for comparing the fractions for samples belonging to the same series (*relative*) but that the *absolute* values of the ferromagnetic fraction correspond to only crude estimations.



**Figure 1.** Ferromagnetic fractions of Ba-doped  $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$  (a) and  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  (b) measured at 2.5 K in 0.25 T.

### 3. Results and discussion

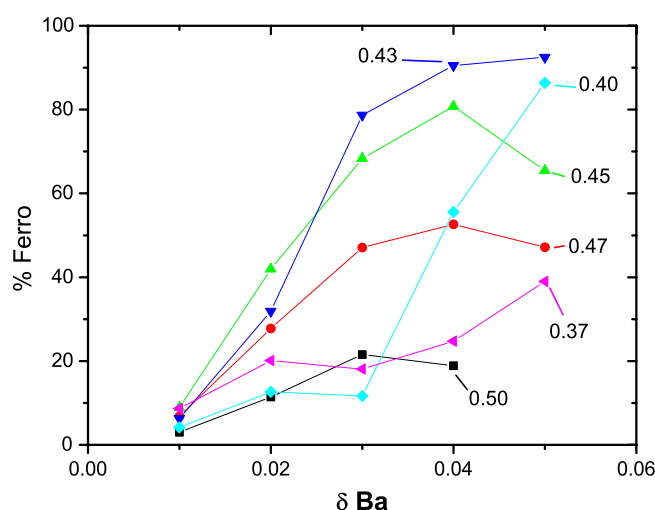
The evolution of the induced ferromagnetic fraction FM (%) versus  $x$  at 2.5 K in 0.25 T for  $\text{Nd}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  (figure 1(a)) exhibits a great similarity with that recently observed for  $\text{Pr}_{1-x}\text{Ca}_{x-\delta}\text{Ba}_\delta\text{MnO}_3$  (figure 1(b)). Indeed we observe that for a given Ba substitution level, in both cases the FM fraction first increases as  $x$  decreases from  $x = 0.50$ , goes through a maximum and then decreases again as  $x$  reaches the limit value  $x = 0.37$ . More importantly, we note the exceptional predisposition of the  $x = 0.43$  composition to ferromagnetism, independently of the nature of the  $\text{Ln}^{3+}$  cation: the maximum FM fraction is indeed obtained for this composition in both Nd and Pr systems, and it is considerable since it reaches 90% in both systems, so that the compounds  $\text{Ln}_{0.57}\text{Ca}_{0.43-\delta}\text{Ba}_\delta\text{MnO}_3$  ( $\delta \sim 0.04$ ) can be considered as full ferromagnets at 2.5 K. Nevertheless some differences appear between the neodymium and praseodymium phases. The barium content that is required to reach this full ferromagnetism is significantly larger for Nd, i.e.  $\delta = 4\%$  (figure 1(a)) than for

Pr, i.e.  $\delta = 2\%$  (figure 1(b)). This difference in the influence of the Ba content upon the ferromagnetic fraction is in fact spectacular, and can easily be evaluated by comparing low doping levels. For instance for 2% Ba doping, a maximum FM fraction of only 40% is reached in the case of  $\text{Nd}_{0.57}\text{Ca}_{0.41}\text{Ba}_{0.02}\text{MnO}_3$  (figure 1(a)) against 90% for  $\text{Pr}_{0.57}\text{Ca}_{0.41}\text{Ba}_{0.02}\text{MnO}_3$  (figure 1(b)). In a more general manner, the maximum ferromagnetic fraction that is reached for a fixed barium substitution level is systematically smaller for Nd than for Pr. Moreover, it can be seen that for low Ba contents ( $<3\%$ ), the maximum FM fraction does not appear for  $x = 0.43$  in the case of Nd but rather for  $x = 0.45$  (figure 1(a)), whereas for Pr all the maximum magnetic fractions are centred on  $x = 0.43$  (figure 1(b)). *Note that this small difference for the optimum composition must be considered cautiously since for these different lanthanides (Pr, Nd) the oxygen stoichiometry may differ slightly leading to a composition shift.*

The great similarity of this system with the Pr one in the absence of magnetic field, especially the exceptional predisposition of the  $x = 0.43$  composition to ferromagnetism, supports our previous model [12], which implies two antagonist effects, the stability of orbital-charge ordered and the local geometric effect of ‘counter-distortion’. The first one takes place at long range in the whole structure and is the highest for  $x = 0.50$  which corresponds to the perfect 1:1 ordering of the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  species and hinders the onset of ferromagnetism. It decreases as  $x$  decreases, i.e. as the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio increases (i.e. deviates from the ideal 1:1 ratio). The ‘counter-distortion’ corresponds to the local increase of the symmetry of the structure which appears around each barium due to its larger size compared to calcium. This effect tends to decrease the Jahn–Teller distortion of the  $\text{Mn}^{3+}$  octahedra that locally surround the  $\text{Ba}^{2+}$  species, and consequently locally destabilize the orbital-charge ordering so that more symmetric ferromagnetic domains are favoured. The strength of the counter-distortion for a given Ba content depends on the number of  $\text{Mn}^{3+}$  Jahn–Teller distorted octahedra surrounding each barium. Consequently, it is the highest for  $x = 0.50$  for which the number of  $\text{Mn}^{3+}$  is the smallest, and decreases as the number of  $\text{Mn}^{3+}$  octahedra increases, i.e. as  $x$  decreases. In summary, the two antagonist effects are maximum for  $x = 0.50$  and both decrease as  $x$  decreases down to  $x = 0.37$ , independently of the  $\text{Ln}^{3+}$  nature,  $\text{Pr}^{3+}$  or  $\text{Nd}^{3+}$ . At  $x = 0.50$ , the stability of charge ordering is very high and predominates over the counter-distortion effect, and consequently the FM fraction remains very low by Ba doping. At decreasing  $x$ , the charge ordering stability decreases more rapidly than the counter-distortion effect in a first step so that the FM fraction increases rapidly up to  $x = 0.43$  (maximum FM fraction). Below  $x = 0.43$  the stability of charge ordering decreases much less than the counter-distortion, so that at  $x = 0.37$  the two effects compensate, leading again to a low FM fraction.

This model also explains why a higher Ba level is required in the case of the Nd system to reach nearly full ferromagnetism in a low magnetic field ( $\sim 4\%$  Ba in the  $x = 0.43$  phase), with respect to the Pr system ( $\sim 2\%$  Ba in the same  $x = 0.43$  compound). Indeed, the perovskite cages of the  $\text{Nd}_{0.57}\text{Ca}_{0.43}\text{MnO}_3$  are more distorted than those of  $\text{Pr}_{0.57}\text{Ca}_{0.43}\text{MnO}_3$ , due to the smaller size of  $\text{Nd}^{3+}$  compared to  $\text{Pr}^{3+}$ . As a consequence, a higher barium content is needed to reach the higher symmetry of the ferromagnetic phase.

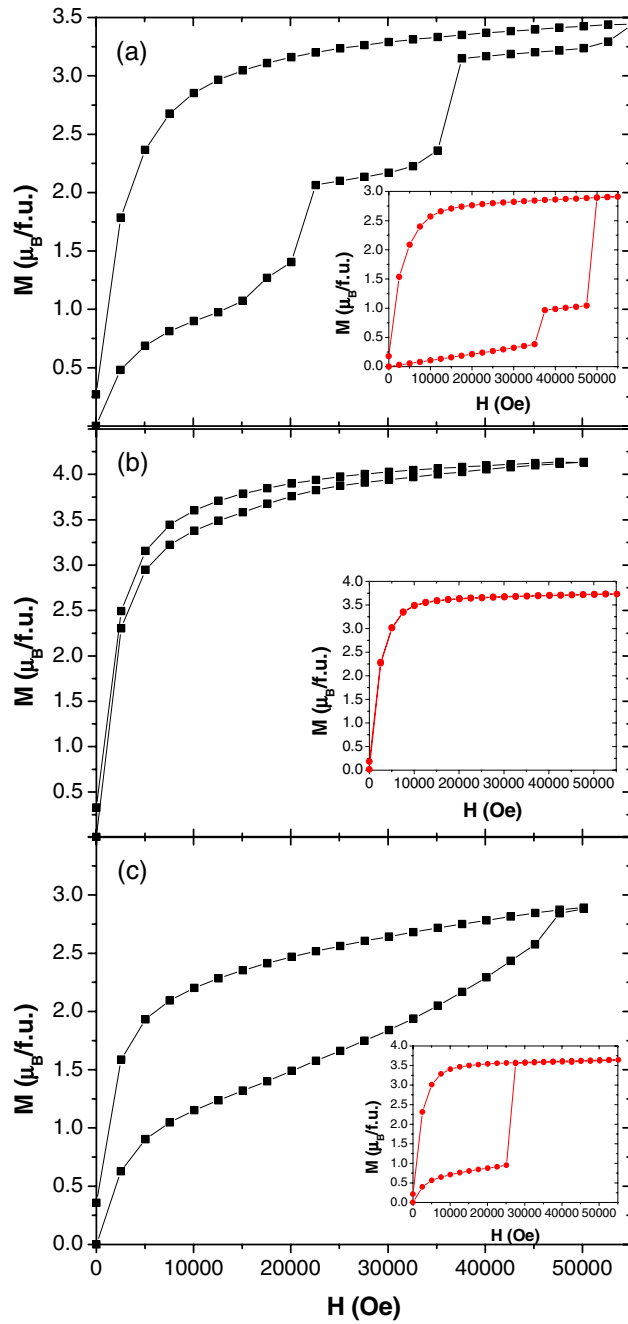
The evolution of the ferromagnetic (FM) fraction versus the barium content  $\delta$  for different  $x$  values (figure 2) corroborates the above model. For  $x = 0.50$ , the FM fraction remains low, 3% to 21%, whatever the barium content. This confirms that for this composition, orbital-charge ordering is particularly stable and hinders large FM fractions to be induced in the absence of magnetic field. As soon as one deviates from the perfect orbital-charge ordering ( $0.43 \leq x \leq 0.50$ ), especially at  $x \sim 0.43$ , one observes a high slope corresponding to the FM fraction increase, which starts at about 2% Ba. In this composition range, both orbital-charge ordering and Jahn–Teller effects are decreased with respect to the limit compositions  $x = 0.50$  and  $0.37$  respectively. As a consequence, a small Ba content ( $>2\%$ ) is sufficient



**Figure 2.** Ferromagnetic fractions versus Ba content ( $\delta$ ) for  $\text{Nd}_{1-x}\text{Ca}_x\text{Ba}_\delta\text{MnO}_3$  measured at 2.5 K in 0.25 T.

to induce a more symmetric structure, and consequently to induce a large FM fraction. In contrast, for  $0.37 < x < 0.43$  the Jahn–Teller effect prevails, due to the higher  $\text{Mn}^{3+}$  content, and the distortion of the structure is higher, so that a higher barium content ( $>4\%$ ) is required to counterbalance this effect and to induce ferromagnetism.

However, in spite of their great similarities, the Nd phases and Pr phases exhibit a significant difference when submitted to a magnetic field. The  $M(H)$  curves registered at 2.5 K, for three compositions,  $x = 0.50, 0.43$  and  $0.37$ , doped with 4% Ba, illustrate these different behaviours (figure 3). The  $M(H)$  curve obtained for  $\text{Nd}_{0.50}\text{Ca}_{0.46}\text{Ba}_{0.04}\text{MnO}_3$  (figure 3(a)) shows the greater field induced effect upon ferromagnetism compared to the isocompositional phase  $\text{Pr}_{0.50}\text{Ca}_{0.46}\text{Ba}_{0.04}\text{MnO}_3$  (inset in figure 3(a)). One indeed observes that the magnetization increases more rapidly with the magnetic field for Nd than for Pr and that the magnetization steps appear at much lower fields, i.e. 2 and 3.5 T for Nd, against 3.5 and 4.8 T for Pr. Importantly, the magnetization value obtained at 3.5 T of  $3 \mu_B$  for Nd is much larger than that obtained for Pr in the same field ( $1 \mu_B$ ). Moreover, the final magnetization obtained in 5.5 T is also significantly higher for Nd ( $3.5 \mu_B$ ) than for Pr ( $2.9 \mu_B$ ). The criteria, discussed above—orbital charge ordering and ‘counter-distortion’ of the Jahn–Teller effect—cannot alone explain this great difference between Nd and Pr. An additional factor must be taken into consideration in the Nd phase, which deals with the existence of effective Mn–Nd magnetic interactions previously emphasized for  $x = 0.50$  by several authors [6, 7, 15, 16]. In agreement with the hypothesis previously proposed by Tokunaga *et al* [6] for  $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ , we can ascribe the higher magnetic moments and lower critical fields observed in a magnetic field for Ba-doped  $\text{Nd}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ , to the existence of field induced Nd moment, which interacts with the Mn moment and destabilizes the CE-type antiferromagnetic structure. This also explains that when the saturation is reached the final magnetic moment of  $\text{Nd}_{0.50}\text{Ca}_{0.46}\text{Ba}_{0.04}\text{MnO}_3$  is higher than the corresponding Pr manganite. The greater ability of Nd phases to exhibit ferromagnetism in a magnetic field compared to Pr phases, decreases rapidly as  $x$  decreases, so that at  $x = 0.43$  the tendency to become ferromagnetic in the field is practically similar for Nd and Pr oxides. For both oxides,  $\text{Nd}_{0.57}\text{Ca}_{0.39}\text{Ba}_{0.04}\text{MnO}_3$  (figure 3(b)) and  $\text{Pr}_{0.57}\text{Ca}_{0.39}\text{Ba}_{0.04}\text{MnO}_3$  (inset in figure 3(b)) the saturation is reached in one step. This confirms, in agreement with our model, that for  $x = 0.43$ ,



**Figure 3.** Magnetization versus magnetic field for  $\text{Nd}_{1-x}\text{Ca}_x\text{Ba}_\delta\text{MnO}_3$  doped with barium (a)  $x = 0.50$   $\delta = 0.04$ , (b)  $x = 0.43$   $\delta = 0.04$ , (c)  $x = 0.37$   $\delta = 0.04$ . The insets correspond to the  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_\delta\text{MnO}_3$  manganites previously studied [12].

the charge-orbital ordering is much weaker and consequently the CE-type antiferromagnetism is also much weaker. Nevertheless, the final magnetization in 5 T is larger for the Nd phase ( $4.1 \mu_B$ ) than for the Pr phase ( $3.5 \mu_B$ ), due to the field induced Nd moment. Finally

for  $x < 0.43$ , the behaviour is reversed, i.e. for the same Ba content the Pr phases show a much higher sensitivity to the magnetic field than the Nd phase. This is illustrated in  $\text{Nd}_{0.63}\text{Ca}_{0.37}\text{Ba}_{0.04}\text{MnO}_3$  (figure 3(c)) which shows a rather regular increase of magnetization with the magnetic field but does not reach saturation at 5 T, displaying a magnetic moment of only  $2.8 \mu_B$ , whereas one observes an abrupt step of the magnetization at 2.5 T for  $\text{Pr}_{0.63}\text{Ca}_{0.33}\text{Ba}_{0.04}\text{MnO}_3$  (inset in figure 3(c)) which practically reaches saturation ( $3.5 \mu_B$ ) in this field. Such an opposite behaviour in the magnetic field, compared to the Ba-doped  $x = 0.50$ -sample, is explained by the fact that, for  $x = 0.37$ , the CE-type AFM is considerably weakened and does not oppose a strong contribution to the appearance of ferromagnetism in a magnetic field. As already stated above, the main force which opposes the ferromagnetism, at  $x = 0.37$ , originates from the Jahn–Teller effect of manganese. The latter can be counterbalanced by increasing the average size of the A-site cation, and it is because  $\text{Pr}^{3+}$  is bigger than  $\text{Nd}^{3+}$ , at the border line of the ferromagnetic domain, that the Ba-doped Pr manganite switches more easily to an FM state than the Ba-doped Nd manganite.

#### 4. Conclusion

The study of the doping of the Ca sites by Ba in the  $\text{Nd}_{1-x}\text{Ca}_x\text{MnO}_3$  manganite shows that similarly to  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  a full ferromagnet is obtained around  $x \sim 0.43$  for a low Ba level ( $\sim 4\%$ ), at 2.5 K. The evolution of the FM fraction versus  $x$  and for various barium contents can be explained in terms of two antagonist effects, the charge-orbital stability which prevails at  $x = 0.50$  and the Jahn–Teller effect which prevails at  $x = 0.37$ . The larger barium content necessary to reach full ferromagnetism for the Nd phase results from the smaller size of  $\text{Nd}^{3+}$  compared to  $\text{Pr}^{3+}$ . The greater ability to induce ferromagnetism by applying a magnetic field in the Nd phase compared to the Pr phase, around  $x = 0.50$ , at low temperature is explained by the existence of a field induced Nd moment which destabilizes the CE-type AFM structure. In contrast, the larger magnetization induced by a magnetic field around  $x = 0.37$  for the Pr phase compared to the Nd phase originates from the larger size of praseodymium.

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