

Training effect by the applied magnetic field in the double-doped $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ system

Li Pi,^{1,2} Jianwei Cai,¹ Quan Zhang,¹ Shun Tan,¹ and Yuheng Zhang^{1,*}¹Structure Research Laboratory, University of Science and Technology of China, Hefei 230026, People's Republic of China²Department of Chemistry, University of Science and Technology of China, Hefei 230026, People's Republic of China

(Received 11 November 2004; revised manuscript received 5 January 2005; published 22 April 2005)

The double-doped $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ system ($0.01 \leq x \leq 0.10$) has been investigated. A training effect by the application of magnetic field is observed. The magnetic hysteresis loop keeps decreasing with the increasing sweep times, suggesting the decrease of the metastable AFM/CO fraction. The irreversible magnetostrictive effects in the volume spin array or the structure mismatch and the elastic energy in the boundary between the phases with a different magnetic state might be the origin of this training effect.

DOI: 10.1103/PhysRevB.71.134418

PACS number(s): 75.60.Ej, 75.30.Kz, 75.47.Lx

I. INTRODUCTION

The charge, orbital and spin degrees of freedom are most important indices of the perovskite manganites. The transformation of the charge, orbital and spin degrees of freedom against external conditions such as temperature, magnetic field, electric field, etc., reflects the changes of the internal interaction and couplings, leading to significant transitions of the physical properties. Furthermore, these degrees of freedom are strongly correlated with each other, which brings forth abundant physical phenomena. Hence, the investigation on the degrees of freedom is a focus of recent physical studies.

The narrow-band manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ is a typical system in which there exists intriguing interplay of the charge, orbital and spin degrees of freedom. It undergoes a charge ordering (CO) transition at $T_{CO} \approx 230$ K and the long-range antiferromagnetic (AFM) ordering is established below $T_N \approx 180$ K.¹ At low temperature, due to the small one-electron bandwidth together with the stable CO state, a large applied magnetic field up to 27 Tesla is needed to induce the insulator-metal (IM) transition.² The Mn site doping is an effective method to suppress the CO state and increase the magnetoresistance. All the doping elements that were investigated to date were found to induce either a partial or a complete charge orbital disordering, leading to a colossal magnetoresistance (CMR) effect under a magnetic field of 7 T.^{3,4} For the dopant with a partially occupied d orbital, the doping induces metallicity and ferromagnetism (FM) in the absence of a magnetic field.⁴⁻⁶ Hébert *et al.* suggest that the dopants with partially occupied d orbital participates in the band formation, broadening the bandwidth so that both metallicity and ferromagnetism are induced.⁷ In the lightly doped system, interesting phenomena have been observed. For instance, for the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Mg}, \text{Ga}$, $0.03 \leq x \leq 0.05$), the magnetic field application at low temperature ($T < 10$ K) induces steplike transitions, not only in the magnetization (M) process from AFM to FM but also in the specific heat and resistivity (ρ).⁸ Another curious result is that the IM transition in the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{M}_x\text{O}_3$ ($M = \text{Cr}, \text{Co}, \text{Ni}$, $\leq x \leq 0.05$) is unstable against thermal cycling. The ferromagnetic phase fraction decreases with increasing ther-

mal cycling.⁹ These results show the richness and complexity of the physics in these systems.

Although the Cr doping in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ has been probed in details,^{4,5,9} we notice that the doping not only induces interaction between the dopant and Mn ions, but also changes the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio, which directly affects the amount of the e_g electrons in the system. Hence, the Cr doped $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ has been prepared. In this system, the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio is fixed to 1:1. The purpose of this design was to check if there is the possibility of better maintaining the CO phase beside the FM domains induced by Cr doping, especially in the heavily doping range. However, the experimental results show that this kind of doping has little difference from normal doping. Nevertheless, interesting phenomenon has been observed during the magnetic hysteresis loops measurements. In this paper, we report an anomalous decrease of the magnetization of $\text{Pr}_{0.505}\text{Ca}_{0.495}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ in the repeated measurement at fixed temperatures. A possible explanation was given.

II. EXPERIMENT

Polycrystalline $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ samples ($0 \leq x \leq 0.10$) were synthesized using the conventional solid-state reaction method. The oxides Pr_6O_{11} , MnO_2 , CaCO_3 , Cr_2O_3 were mixed in stoichiometric proportions and heated in air at 900 °C for 24 h and 1380 °C for 24 h with intermediate grinding for better crystallization. Afterwards the powder was pressed into pellets and sintered in air at 1380 °C for 30 h. Finally the samples were cooled down to room temperature with the furnace. Powder x-ray-diffraction patterns obtained on a Japan Rigaku $D/\text{max-}\gamma\alpha$ rotating powder diffractometer show that the samples are single phase without any detectable impurities. Energy dispersive spectroscopy (EDS) analysis show that the samples are homogeneous in the limit of accuracy of the technique.

The magnetization curves were recorded on a Lakeshore VSM-9300 vibrating sample magnetometer. The resistivity of the samples was measured using the standard four-probe method. In order to avoid the thermal cycling effect,⁹ each measurement was performed on a fresh sample. To measure the magnetic hysteresis loops, the fresh sample was cooled

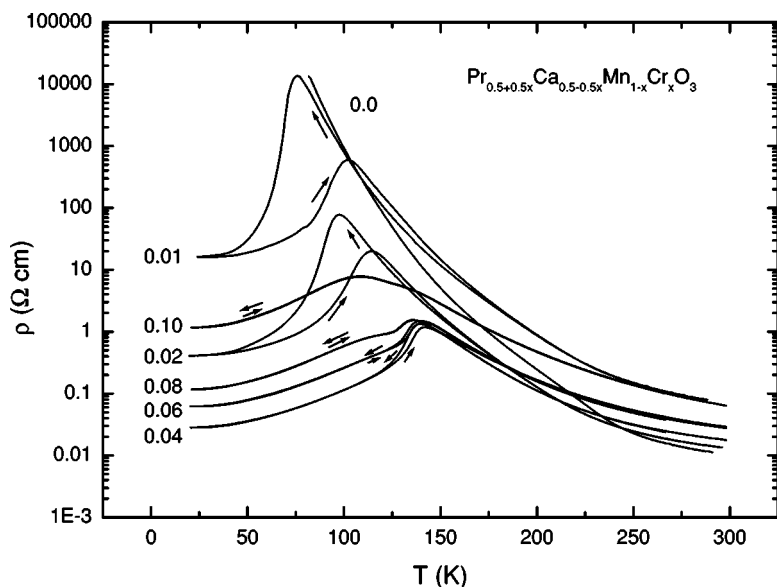


FIG. 1. Temperature dependence of resistivity of $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$.

directly from room temperature to the set temperature. The specific heat was measured in the temperature range of 80 K to 300 K.

III. RESULTS AND DISCUSSIONS

Figure 1 presents the temperature dependence of resistivity for the $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ samples. For the undoped sample, the curve shows a jump at the CO transition temperature $T_{CO}=248$ K and increases dramatically with cooling, just as other groups reported. As the doping concentration increases, the CO transition becomes more and more unclear on the ρ - T curves. For $x \geq 0.04$, the inflection point becomes hard to identify. A first order IM transition^{9,10} occurs early with 1% Cr doped. The transition temperature T_{IM} in the cooling process, 76 K, differs from that in the warming process, 102 K, showing an obvious hysteresis. With more Cr doped ($x \leq 0.04$), T_{IM} increases and the peak resistivity ρ_{max} drops. As the Cr content exceed 6%, ρ_{max} starts to increase and T_{IM} decreases. The hysteresis is reduced monotonously with doping. For the samples with $x=0.08$ and 0.10, the cooling curves coincide with the warming curves very well. Figure 2(a) shows the temperature dependence of the specific heat for all the samples. The C/T - T curves are displayed in Fig. 2(b). Clear bumps can be seen at the temperatures corresponding to the CO transition and PM-AFM transition for the undoped sample. With doping, these bumps vanish quickly. And a peak which corresponds to the IM transition appears. The peak temperature is close to the T_{IM} of the cooling process (Table I). The exception is the $x=0.01$ sample, which does not exhibit the peak corresponding to the IM transition. It is because in the specific heat experiment, the $x=0.01$ sample was only cooled down to liquid nitrogen temperature and did not enter the metallic state (the T_{IM} in the cooling process is 76 K). The magnetization measurement results coincide with the resistivity and specific heat data quite well. The temperature dependence of magnetization is given in Fig. 3. The sample with $x=0$ exhibits a peak on the M - T curve at 250 K, just near T_{CO} . With

Cr doping, the peak at T_{CO} shifts to lower temperature and becomes invisible for $x \geq 0.04$, suggesting that the long-range OO/CO has been destroyed. A clear FM state appears at the beginning of the doping. The transition temperatures T_C and the magnetization values are list in Table I to compare. It can be seen that the T_C 's from the M - T curves which were registered in the warming process are in accord with the T_{IM} 's from the warming curves of the resistivity measurements. For the sample with $x=0.10$, T_C is close to the shoulder temperature on the ρ - T curve. All the results indicate that the charge ordering is gradually suppressed by the Cr doping and the AFM state becomes short range. The FMM clusters

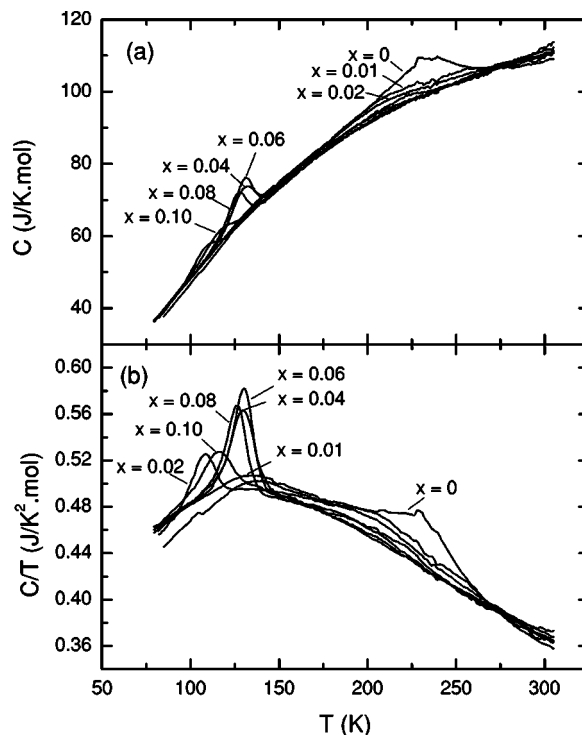


FIG. 2. Temperature dependence of the specific heat of $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$.

TABLE I. The comparison of the IM transition temperature (T_{IM}), peak resistivity (ρ_{max}), peak temperature of specific heat (T_p), Curie temperature (T_C) and magnetization under 1.45 T at 5 K (M_0) of $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ samples ($0.01 \leq x \leq 0.10$).

x	T_{IM} (K)		ρ_{max} (Ω cm)		T_p (K)	T_C (K)	M_0 (μ_B)
	Cooling	Warming	Cooling	Warming			
0.01	76	102	13990	597.5	-	110	0.5
0.02	97	114	77.83	20.00	108	115	1.5
0.04	139	142	1.337	1.184	129	142	2.6
0.06	140	141	1.482	1.390	131	140	2.4
0.08	136	136	1.544	1.529	126	138	2.1
0.10	108/130 ^a	108/130 ^a	7.741	7.851	116	127	2.0

^aThe latter value is the shoulder temperature on the ρ - T curve.

are induced. The FMM fraction increases rapidly with doping, reaches its maximum at $x=0.04$ and decreases with further doping.

Compared to previous work,^{4,5} the resistivity and magnetization results have been proved to be similar to those of the normally Cr doped system. One possible reason is that there is some oxygen deficiency which makes it impossible to control the $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio. Another fact is that $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ compounds are charge ordered insulators over a wide x range ($0.3 \leq x \leq 0.7$).² So the physical properties of the (Pr,Ca) MnO_3 system are not sensitive to the Mn^{3+} concentration as in the (La,Ca) MnO_3 system.

In order to explore the hysteresis region more clearly, the magnetic hysteresis loops for the $x=0.01$ sample which has the largest hysteresis area in the ρ - T curve have been recorded at various temperatures. Figure 4 shows the M - H curves. The numbers and the arrows in the figure indicate the sequence and the direction of field sweep. At 5 K, with the application of H , the M increases rapidly, showing the FM characteristic. Then the magnetization increases almost linearly with the intermediate field. As the applied field exceeds 3 T, the M exhibits a faster increase, showing a metamagnetic transition. In the down-sweep process, the M stays at the high value until the H decreases to zero, showing a loop in the first quadrant. In the third sweep process, in which the

H was applied in the opposite direction, the absolute value of M increases directly to the high value with the increase of $|H|$. As the H goes back to zero in the fourth process, the M superposes the track in the third process. And the track of the fifth sweep process coincides with that of the second process instead of that of the first process. In the case of $T=20$ K and 35 K, the system experiences similar changes to those at 5 K with the application of H . The difference is that in the higher temperature case, the M value in the fifth sweep process is smaller than in the second process, but higher than in the first sweep. With temperature increasing further ($T=65$ K), the different up-sweep processes become nearly superposed. The M - H curve is a symmetric loop. At higher temperatures ($T \geq 100$ K), the system does not exhibit the FM behavior anymore. The M increases linearly with H at low field, then displays a metamagnetic transition. At 250 K, the system exhibits paramagnetic behavior in the range of $H \leq 6$ T.

The above experimental results can be well explained by an extended de Gennes model¹¹ proposed by Bärner *et al.*¹² if we regard the T_{CO} (230 K) and the T_C (110 K) as the disorder-order transition temperature (T_n) and order-order transition temperature (T_1), respectively. According to this model, as soon as some Zener carriers are present in some antiferromagnetic lattices, the ground state spin arrangement are distorted. The distortion usually correspond to a canting

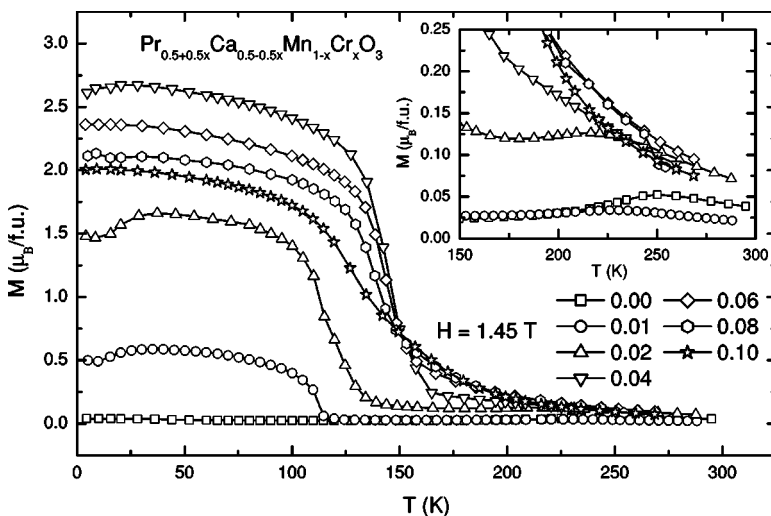


FIG. 3. Magnetization measured as a function of T at an applied field of 1.45 T for the $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ samples. The high temperature part is enlarged and shown in the inset.

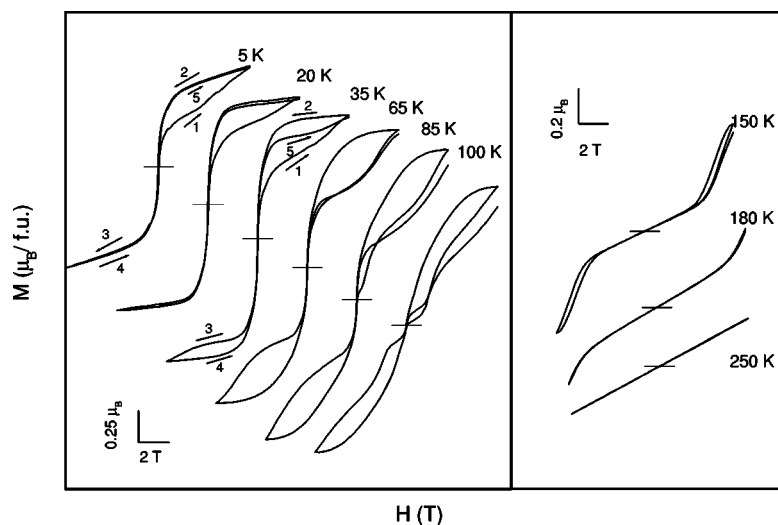


FIG. 4. M - H curves at various temperatures for a $\text{Pr}_{0.505}\text{Ca}_{0.495}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ sample. The numbers and the arrows indicate the sequence and the direction of the field sweep.

of the sublattices, which is stable up to a well-defined temperature T_1 . Above T_1 the system is either antiferromagnetic or ferromagnetic, depending upon the relative amount of mobile electrons. T_1 can be shifted by the applied magnetic field. Hence, the metamagnetic M - H hysteresis loops will occur for $T_1 < T < T_n$.

However, the extended de Gennes model is based on a system which is homogeneous with only slightly randomized phases inside. While in the Cr doped system, phase separation has been evidenced by different groups. With a dark-field image of $\text{Nd}_{1/2}\text{Ca}_{1/2}\text{Mn}_{0.97}\text{Cr}_{0.03}\text{O}_3$, Moritomo *et al.*¹³ demonstrate that the AFM CO microdomains with a typical size of 20–50 nm can be clearly observed in the FM domains at 120 K. Mahendiran *et al.*⁵ also show that within the FM region ($T < 140$ K) of the $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ system, ordering of charges appears as superlattice reflections in electron diffraction pattern at positions q from the main Bragg peaks. Therefore, it seems more reasonable to consider our system at low temperature as a coexistence of FM phase and short-range AFM/CO domains.

Within the phase separation scenario, the M - H results can be well understood. At 5 K, the system is a mixture of the FM phase and AFM/CO domains. The interaction in some of the AFM domains is still strong. But in other domains, it might be weak. When the applied field is small, these “weak” domains remain in their AFM state. While a relatively large magnetic field is applied, the AFM interaction can be destroyed and the spins can be flipped. Therefore at $H < 3$ T, the M - H curve only exhibits the behavior of the FM domains. When the applied field exceeds 3 T, the spins in the “weak” AFM domains are flipped to the field direction, leading to an obvious increase of the magnetization. The fact that the magnetization is not saturated and the value at 6 T is much smaller than the theoretically calculated saturation magnetization demonstrates that not all the AFM domains has been transformed. There are still “strong” AFM domains inside the system. As the field is withdrawn, the original AFM domains which have been melt by the field now remains ferromagnetic under the influence of the ferromagnetic interaction in the system. So the system does not exhibit metamagnetic transition in the following sweep processes.

Hence, the M - H curve can be regarded as the superimposition of a FM loop and an asymmetric irreversible metamagnetic transition loop of the CO domains. For $T=20$ K and 35 K, after the H increases to 6 T and decreases back to zero, parts of the original CO domains remain their FM spin arrangement which is obtained at high field, and the others transform back to the AFM state. At higher temperatures ($T=65$ K, 85 K), the FM interaction in the system becomes weaker. The ferromagnetic aligned spins in the original CO domains cannot remain their state without the help of the external field. The M - H curves are symmetric metamagnetic loops. For $T \geq 100$ K, the FM order begins to transform to the PM state, and the magnetization increases linearly with a low applied field. On the other hand, the short-range AFM/CO domains still exist in the system. As a consequence, the metamagnetic transition occurs at high field. At $T \geq 250$ K, the system is in the PM state. The M - H curve is a straight line in the range of $H \leq 6$ T.

What should be noted is that in the temperature range of $65 \text{ K} \leq T \leq 150 \text{ K}$, especially for $T=100$ K, the M values in the last up-sweep processes are smaller than in the first up-sweep processes. In order to make it clearer, the repeated magnetic hysteresis loops have been recorded. The fresh samples were cooled directly from room temperature to the set temperature. The repeated sweeps at $T=75$ K, 100 K, 120 K, and 150 K are displayed in Fig. 5. The number of up-down sweeps is denoted by the numeric 1,2,3, etc. Take the case of $T=100$ K as an example; the M value at 6 T in the first up-down sweep reaches $1.1\mu_B$. In the second sweep, the field is applied in the opposite direction. When H reaches -6 T, the M value is $-1.0\mu_B$. In the third sweep, the maximum M value is decreased to $0.94\mu_B$. And in the fifth sweep, the M value at 6 T is only $0.85\mu_B$. The magnetic hysteresis loop and the absolute M value at ± 6 T keeps decreasing with the increasing sweeping times. Similar situations occur in other loops. With temperature increasing, this training effect becomes less prominent. At $T \geq 180$ K, the M in the first two sweeps superposes that in the following sweeps. The abnormal phenomenon occurs just in the temperature hysteresis range which can be clearly seen in the ρ - T curve in Fig. 1.

Note that the decrease of the loops occurs at $H > 3$ T. The part before the metamagnetic transition does not change with

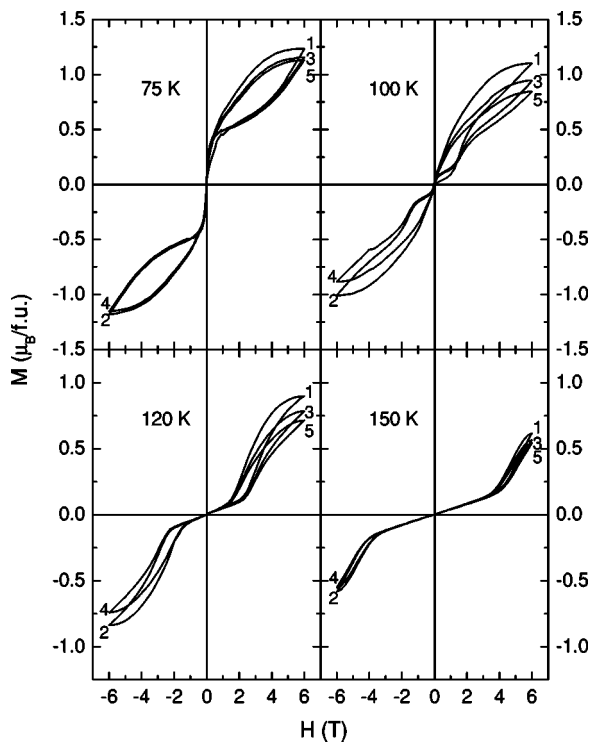


FIG. 5. Repeated M - H loops at various temperatures for the $\text{Pr}_{0.505}\text{Ca}_{0.495}\text{Mn}_{0.99}\text{Cr}_{0.01}\text{O}_3$ sample. The numbers indicate the sequence of the up-down sweeps.

the repeat of the field sweeping. It suggests that the metastable AFM fraction is decreased with the repeated sweeps of the magnetic field. As we mentioned before, the system is believed to be a coexistence of FM domains (or PM phase if the temperature is higher than T_C), metastable AFM domains and relatively stable AFM domains. The M - H curve is mainly contributed by the FM/PM domains and the metastable AFM domains. The fact that the low field part remains unchanged while the high field loop decreases indicates that it is the metastable AFM domains instead of the FM/PM domains that decreases in number with the field cycling. These metastable domains transform to the more stable AFM state after the field sweep, leading to less of a contribution for the magnetization. The reason why the metastable domains decrease in number is not clear yet. Nevertheless, although this training effect is caused by the application of a magnetic field and different from the thermal cycling effect, as reported in other groups' works,^{9,14} the origin might be similar. In this kind of phase separation system, the AFM phase is a more stable one in this temperature range. Due to

the different lattice parameters between the domains with a different magnetic state,^{15,16} surely there exists the significant structure distortions near the boundary between different domains. In the thermal cycling effect, the Jahn-Teller distortion in the interfacial regions increases upon thermal cycling. As a result, the interfacial elastic energy increases which impedes the growth of the ferromagnetic phase and leads to the magnetization decrease.⁹ In other words, in the phase separation system, the repeated transitions between the different magnetic state would favor the growth of the more stable phase. In the training effect reported by us, the transition is driven by the field sweep. With the field sweep, the FM domains do not experience the magnetic transition so that the fraction of the FM phases does not change. On the contrary, the metastable domains experience the transformation from AFM to FM and back to the AFM state. This process is likely helpful to combine these small, "weak" domains into the larger, more stable AFM domains and consequently leads to the decrease of magnetization. The irreversible magnetostrictive effects in the volume spin array is another possible explanation for this anomalous training effect. This phenomenon is also observed in the higher-doped $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ samples. In fact, other system such as $\text{Nd}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ exhibits similar behaviors too,¹⁷ suggesting that this training effect is a common phenomenon of the phase separation system.

IV. CONCLUSIONS

In summary, the double-doped $\text{Pr}_{0.5+0.5x}\text{Ca}_{0.5-0.5x}\text{Mn}_{1-x}\text{Cr}_x\text{O}_3$ system ($0.01 \leq x \leq 0.10$) has been investigated. The magnetic hysteresis loops for the $x=0.01$ sample were carefully studied. A new training effect by the application of magnetic field is observed. The magnetic hysteresis loop keeps decreasing with the increasing sweep times, suggesting the decrease of the metastable AFM/CO fraction. The structure mismatch and the elastic energy in the interface between domains of different magnetic state or the irreversible magnetostrictive effects in the volume spin array might be the origin of this training effect.

ACKNOWLEDGMENTS

This work was supported by the National Nature Science Foundation of China (No. 10334090), the State Key Project of Fundamental Research, China (001CB610604), and the China Postdoctoral Science Foundation. The authors gratefully acknowledge the support of K. C. Wong Education Foundation, Hong Kong.

*Corresponding author. Electronic address: zhangyh@ustc.edu.cn

¹Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, *Phys. Rev. B* **53**, R1689 (1996).

²M. Tokunaga, N. Miura, Y. Tomioka, and Y. Tokura, *Phys. Rev. B* **57**, 5259 (1998).

³A. Maignan, F. Damay, C. Martin, M. Hervieu, and B. Raveau,

Mater. Res. Bull. **32**, 965 (1997).

⁴B. Raveau, A. Maignan, and C. Martin, *J. Solid State Chem.* **130**, 162 (1997).

⁵R. Mahendiran, M. Hervieu, A. Maignan, C. Martin, and B. Raveau, *Solid State Commun.* **114**, 429 (2000).

⁶B. Raveau, S. Hébert, A. Maignan, R. Frésard, M. Hervieu, and

- D. Khomskii, J. Appl. Phys. **90**, 1297 (2001).
- ⁷S. Hébert, A. Maignan, C. Martin, and B. Raveau, Solid State Commun. **121**, 229 (2002).
- ⁸S. Hébert, V. Hardy, A. Maignan, R. Mahendiran, M. Hervieu, C. Martin, and B. Raveau, J. Solid State Chem. **165**, 6 (2002).
- ⁹R. Mahendiran, B. Raveau, M. Hervieu, C. Michel, and A. Maignan, Phys. Rev. B **64**, 064424 (2001).
- ¹⁰M. Uehara, S. Mori, C. H. Chen, and S. -W. Cheong, Nature (London) **399**, 560 (1999).
- ¹¹P. -G. de Gennes, Phys. Rev. **118**, 141 (1960).
- ¹²K. Bärner, P. Mandal, and R. V. Helmolt, Phys. Status Solidi B **223**, 811 (2001); K. Bärner, and E. A. Zavadskii, *ibid.* **232**, 356 (2002).
- ¹³Y. Moritomo, A. Machida, S. Mori, N. Yamamoto, and A. Nakamura, Phys. Rev. B **60**, 9220 (1999).
- ¹⁴R-W. Li, J-R. Sun, Qi-A. Li, Z-H. Cheng, Z-H. Wang, S-Y. Zhang, and B-G. Shen, J. Phys.: Condens. Matter **13**, 1973 (2001).
- ¹⁵H. Kuwahara, Y. Tomioka, A. Asamitsu, Y. Moritomo, and Y. Tokura, Science **270**, 961 (1995).
- ¹⁶P. G. Radaelli, D. E. Cox, M. Marezio, S.-W. Cheong, P. E. Schiffer, and A. P. Ramirez, Phys. Rev. Lett. **75**, 4488 (1995).
- ¹⁷J. Fan, L. Pi, and Y. Zhang, to be published.