Instability of metal-insulator transition against thermal cycling in phase separated Cr-doped manganites

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$Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ ($x=0.015–0.05$) undergoes an insulator-metal (I-M) transition below a temperature T_p driven by percolation of ferromagnetic metallic clusters in a charge ordered insulating matrix. Surprisingly, the I-M transition in these compounds is unstable against thermal cycling: T_p decreases and the resistivity at T_p increases upon temperature cycling between a starting temperature T_S and a final temperature T_F and changes are larger for smaller x. The resistivity transition to the low temperature metallic state in $x=0.015$ can be completely destroyed by thermal cycling in absence of magnetic field as well as under $H=2$ T. Magnetization measurements suggest that the ferromagnetic phase fraction decreases with increasing thermal cycling. Contrary to the thermal cycling induced effect, isothermal aging causes a slow decrease of resistivity as a function of time. We suggest that increase of strains in the ferromagnetic-charge ordered interface during thermal cycling could be a possible origin of the observed effect.

I. INTRODUCTION

Over the past few years, manganites of the general formula $R_{1-x}A_xMnO_3$ have been studied extensively.[1] Although primary interest in these compounds is motivated by the discovery of colossal magnetoresistance, understanding the physical properties even in absence of magnetic field is still far from clear. In particular, the behavior of the resistivity (ρ) is intriguing. The well studied $La_{0.67}Ca_{0.33}MnO_3$ compound with hole density of $n_h=0.33$ per Mn exhibits a paramagnetic insulator to a ferromagnetic metal transition upon cooling from high temperature at $T_p=T_C$ where T_C is the ferromagnetic Curie temperature. For the same hole concentration, the residual resistivity spans over six orders of magnitude and T_p shifts down, either with different choices of the rare earth (R) and the alkaline (A) ions[2] or by only varying their fraction as in $(La_{1-y}Pr_y)_{0.67}Ca_{0.33}MnO_3$.[3] The paramagnetic state of some other manganites like $La_{0.7}Sr_{0.3}MnO_3$ is metallic[4] instead of insulating. Metallic-like resistivity behavior ($d\rho/dT>0$) in the paramagnetic state was also reported in $R_{1-x}Ca_xMnO_3$ for $x=0.8–0.98$ and $R=$ Pr, Nd, Sm, etc.[5] Charge localization due to random Coulomb potentials of R^{3+}, A^{2+} ions and spin disorder scattering alone are inadequate to understand these results and other polaronic mechanisms involving strong electron-phonon-spin coupling have to be considered.[6]

One of the peculiar aspects of the manganites with high residual resistivity is that T_p occurs much below T_C in contradiction to the double exchange mechanism which associates the onset of metallic conduction to the ferromagnetic alignment of Mn spins ($T_p=T_C$). There are growing experimental evidences that in most, if not all of the compounds with lower T_P (<150 K), insulator-metal transition is driven by percolation of the ferromagnetic metallic clusters in either paramagnetic or charge ordered insulating background.[7,8,10–12] The huge hysteresis in resistivity of these percolation driven compounds suggests that the transition is of first order. However, kinematics of the transition is largely unknown except for two cases. Babushkina *et al.*[13] found that low the temperature zero field resistivity of $(La_{0.5}Nd_{0.5})_{0.7}Ca_{0.3}MnO_3$ thin film relaxes to lower values as a function of time. Anane *et al.*[14] reported that the magnetic field driven metallic state of $Pr_{0.67}Ca_{0.33}MnO_3$ is unstable and the resistivity at a given temperature jumps abruptly from a low to a high value at a particular value of time after the removal of external magnetic field. The transition in both of these compounds is of isothermal type, involving growth of ferromagnetic metallic nuclei as a function of time in a charge ordered matrix in the former compound and vice versa in the latter. It is not clear whether time dependent growth of the low temperature phase is the general aspect of the first order transition in manganites. In this background, we have chosen $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ compounds which are best known for the spectacular insulator-metal transition shown by them in absence of a magnetic field.[9] The insulator-metal transition in these compounds is due to the percolation of the ferromagnetic clusters in the charge ordered antiferromagnetic matrix and the ferromagnetic phase fraction can be controlled by changing the composition (x) as well as the applied field (H) thus allowing us to study systematically.[10–12] We will report a new form of insulator-metal transition in this series: The insulator-metal transition is unusually unstable with respect to thermal cycling in absence and in the presence of a magnetic field.

II. EXPERIMENT

We measured four probe resistivity of polycrystalline $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ ($x=0.015,0.02,0.025,0.03$) in absence of magnetic field and in presence of $H=2$ T and 5 T. The temperature was cycled down and up several times from the starting temperatures $T_S=350$ K, 300 K, 250 K, 160 K, 100 K, 60 K to the final temperature $T_F=5$ K at a constant sweep rate of 2.5 K/min. Magnetization under a weak magnetic field of $H=1$ mT and also under $H=2$ T were mea-
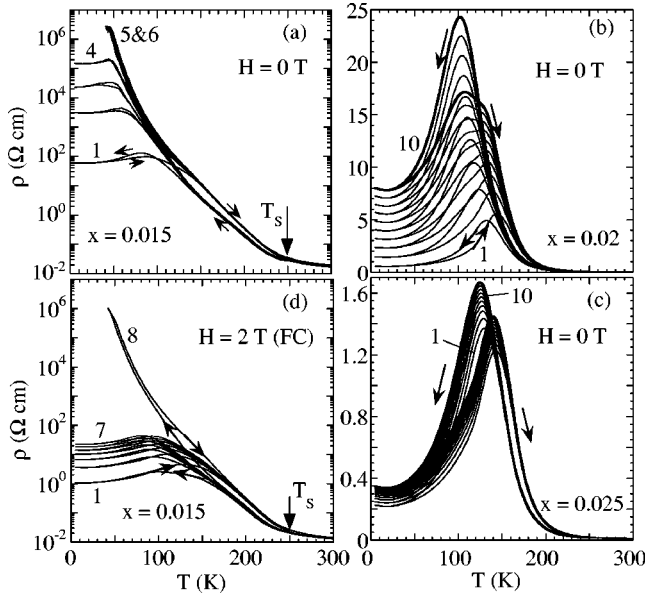
FIG. 1. Resistivity of $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ in number of thermal cycling under $H=0$ T for $x=0.015$ (a), 0.02 (b), 0.03 (c) and under $H=2$ T for $x=0.015$ (d). $T_S=$ starting temperature for thermal cycling. Arrows indicate the direction of temperature sweep.

FIG. 2. Resistivity of $Pr_{0.5}Ca_{0.5}Mn_{0.985}Cr_{0.015}O_3$ in different thermal cycles under $H=0$ T for $T_S=100$ K (main panel) and $T_S=160$ K (inset). (b) Resistivity under partial thermal cycling from a fixed $T_S=250$ K to a varying T_F from 100 K by a step of -10 K. Inset: Time dependence of resistivity at $T=60$ K in different thermal cycles.

sured down and up in between $T_S=300$ K, 250 K, 150 K, and $T_F=5$ K.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows $\rho(T)$ of $x=0.015$ under $H=0$ T when temperature is cycled down and up from $T_S=250$ K to $T_F=5$ K. The number of cycles is denoted by numeric 1,2,3 etc. The sample was not taken out the cryostat prior to the completion of all the thermal cycles. After the 1st cycle 300 K→5 K→300 K, T is reduced to T_S. In the 1st cycle, ρ raises rapidly around 230 K due to charge-orbital ordering and changes from insulating ($d\rho/dT<0$) to metal-like ($d\rho/dT>0$) behavior below $T_p=84$ K. $\rho(T)$ is hysteretic with warming curve below and above the cooling curve for $T<T_p$ and $>T_p$ respectively, and both curves merge for $T>280$ K. During the 2nd cycle, T_p shifts down to 74 K and the value of the resistivity ρ_p at T_p increases by more than a factor of 10. Upon further thermal cycling, ρ_p increases to $\approx 1.95\times10^5$ and T_p decreases to 45 K in the 4th cycle and ρ exceeds more than 10^6 Ω cm at 40 K in the 5th and 6th cycles. This effect is dominant only for $T<T_p$ and T close but above T_p but for $T>100$ K, all $\rho(T)$ curves overlap on each other. The variations of T_p and ρ_p with number of cycles will be presented later in Fig. 3. The so obtained insulating state is stable and does not revert to the original behavior (1st cycle) when the sample is heated to 300 K and cycled between 300 K and 5 K several times. However, if the sample is air annealed at 1273 K for five hours, the 1st cycle is reproducible with identical T_p and ρ_p. It should be mentioned that the virgin sample was originally annealed at 1773 K,[9] and annealing at 1273 K after thermal cycling is sufficient to remove any residual strain developed. We found that a shorter annealing time, for example 3 hours at 1273 K,
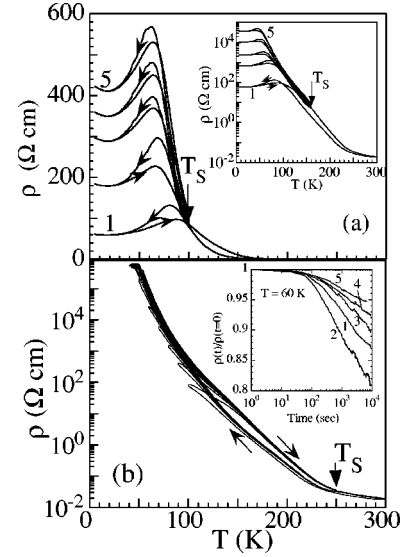
reintroduces the insulator metal transition but with different T_p and ρ_p. A detailed annealing time dependence of the insulator metal transition is under investigation and will be published in the future. For subsequent measurements to be reported in this paper, we used small bars (3 mm×1 mm ×1 mm) cut from a single big virgin pellet. Although the insulator-metal transition in manganites is known to be sensitive to chemical doping, pressure, magnetic field, etc.,[1−9] a destruction of the insulator-metal transition just by thermal cycling is reported. Our results mimics the behavior of $(La_{1-y}A_y)_{0.67}Ca_{0.33}MnO_3$ ($y=Pr$, Y, etc.) series whose T_p decreases and ρ_p increases with increasing content of smaller Y rare earth ions.[3]

The observed effect is strongly dependent on the composition and decreases with increasing x. Figure 1(b) shows ρ of $x=0.02$. This compound exhibits higher T_p (= 120 K while cooling) and nearly ten times lower ρ_p (=4.8 Ω cm while cooling) than $x=0.015$ ($T_p=84$ K and ρ_p =136 Ω cm while cooling). There is a systematic trend in the behavior of ρ_p (warm) and T_p (warm) with increasing the number of cycles: ρ_p (warm) is comparable to ρ_p (cool) in the 2nd cycles but becomes much lower than cooling as the number of cycles increases. The weak shoulder in ρ(warm) which develops around 105 K in the 3rd cycle becomes a prominent maximum in the 10th cycle. As for $x=0.015$, resistivity curves in different cycles overlap on each other for $T\gg T_p$. Compared to variations by several orders of magnitude in ρ_p (cool) for $x=0.015$, ρ_p (cool) changes only by a factor of 5 in $x=0.02$, even in 10th cycle and by less than a factor of 0.8 in $x=0.03$ [see Fig. 1(c)]. The resistivity of $x\geq0.03$ is unaffected by thermal cycling (not shown here). Figure 1(d) shows $\rho(T)$ of $x=0.015$ under $H=2$ T. We can clearly see the increase of the resistivity with increasing the
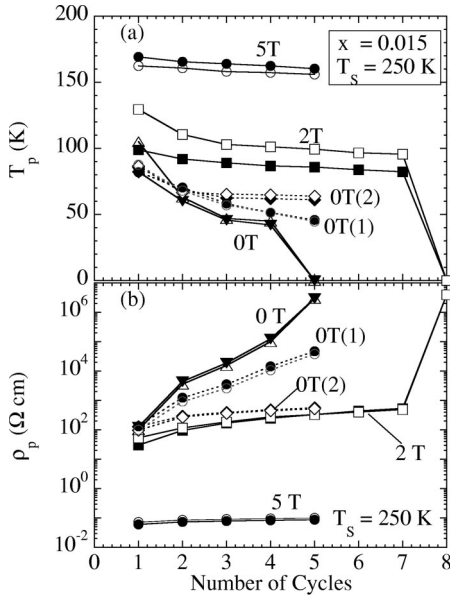
FIG. 3. Variation of T_p (a) and ρ_p (b) with number of cycles during cooling (closed symbols) and warming (open symbols) for $T_S = 250$ K under $H = 0$ T, 2 T, and 5 T for $x = 0.015$. O(1) and O(2) respectively stand for $T_S = 160$ K and 100 K for $H = 0$ T.

FIG. 4. Temperature dependence magnetization of $Pr_{0.5}Ca_{0.5}Mn_{0.985}Cr_{0.015}O_3$ under $H = 1$ mT for $T_S = 250$ K (a) and $T_S = 160$ K (inset). $M(T)$ under 2 T in 1st and 8th cycle (b) and field dependence of magnetization in 1st and 8th cycles (inset). H_c: critical field for metamagnetic transition.

number of cycles and the insulator-metal transition is abruptly lost in the 8th cycle. A comparison of Figs. 1(a) and 1(d) suggests that it is impossible to predict what should be the value of residual or peak resistivity before the sample loses metallic behavior. In the rest of the paper we focus on $x = 0.015$ which shows the most dramatic effect.

We also investigated whether the observed effect in $x = 0.015$ is dependent on the starting temperature T_S. The resistivity curves for $T_S = 350$ K, 300 K, and 200 K are identical to the data for $T_S = 250$ K and hence we do not present them here for the lack of space. The main panel of Fig. 2(a) shows $\rho(T)$ for $T_S = 100$ K and the inset shows data for $T_S = 160$ K. The value of ρ_p in the 5th cycle decreases from $\approx 3 \times 10^4$ Ω cm for $T_S = 160$ K to ≈ 575 Ω cm for $T_S = 100$ K and for $T_S = 60$ K (not shown here) whereas ρ increases by less than a factor of 1.2. These results point to the fact that the number of cycles needed to destroy insulator-metal transition increases with lowering temperature below 200 K. Instead of varying T_S, we also investigated the effect of varying T_F. Figure 2(b) shows $\rho(T)$ for $x = 0.015$ with $T_S = 250$ K but T_F decreasing from 100 K to 10 K instep of 10 K. In none of the cycles, transition to metallic state is realized. Figure 3 summarizes the variations of T_p and ρ_p with the number of cycles and T_S for $x = 0.015$ in presence and absence of magnetic field.

A doubt could be raised whether the increase of ρ is caused by the elapse of time during thermal cycling. To verify this point we measured time dependence of the resistivity at 60 K in different cycles on a sample not submitted to thermal cycling earlier. The result presented in the inset of Fig. 2(b) in a normalized form $[\rho(t)/\rho(t=0)$, where $\rho(t)$ is the resistivity after t seconds] clearly suggests that ρ decreases with time as found by Kimura et al.[12] in

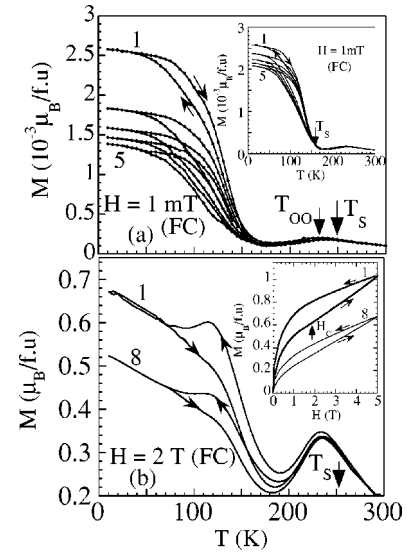$Nd_{0.5}Ca_{0.5}Mn_{0.98}Cr_{0.02}O_3$. This confirms that the observed increase of the resistivity is purely a temperature driven effect. Thus, two different antagonist mechanisms seems to act in thermal cycling and isothermal aging effects. The isothermal aging effect is possibly caused by growth of ferromagnetic clusters in size with time.[12]

To understand the origin of the unstable I-M transition induced by thermal cycling, we carried out magnetization measurements. The main panel of Fig. 4(a) shows $M(T)$ of $x = 0.015$ under $H = 1$ mT for $T_S = 250$ K. The peak around 230 K is caused by charge-orbital ordering. Upon lowering temperature further ferromagnetic clusters form below 150 K. Charges are itinerant within these clusters by double exchange mechanism but the resistivity does not decrease as these clusters are isolated. As T decreases further intercluster interactions increase and when a percolating path between ferromagnetic clusters is established around 84 K, $\rho(T)$ decreases as in Fig. 1(a). Figure 4(a) clearly shows that the ferromagnetic transition broadens in temperature and its phase fraction decreases each time with temperature cycling. Interestingly, M decreases by about 30% between the first two cycles but the overall change between the 1st and 5th cycles is only of about 46%. It should be noted that M does not go to zero in the 5th cycle whereas metallic behavior is lost in resistivity [see Fig. 1(a)]. When $T_S = 160$ K, the overall decrease between the 1st and 5th cycles is only 19% [see inset of Fig. 4(a)].

Figure 4(b) shows $M(T)$ measured under a field of 2 T in the field cooled mode and the inset shows $M(H)$ at 10 K made under zero field cooled mode. $M(H)$ in the 1st cycle [see inset in Fig. 4(b)] shows a two phase behavior, one due to gradual alignment of ferromagnetic clusters in the field direction below 1.5 T and another due to field induced canting of spins in antiferromagnetic background above 1.5 T.

The observed total magnetization is $M_{obs} = f_m M_{FM} + (1 - f_m) M_{AF}$, where f_m and $1 - f_m$ are the volume fractions of the ferromagnetic and the antiferromagnetic phases with saturation magnetic moments M_{FM} and M_{AFM}, respectively. The spin only saturation moment of the Mn site cation is $3.485 \mu_B$ if spins of Cr^{3+}, Mn^{3+}, Mn^{4+} ions are parallel and $3.395 \mu_B$ if the moment of Cr^{3+} ion is reversed as suggested earlier.[10] Assuming that the magnetization of the ferromagnetic phase completely saturates at 1.5 T, and the field induced canting of antiferromagnetic moment is negligible below this field, we can estimate the ferromagnetic phase fraction $f_m = M_{obs}/M_{FM} = 0.582/3.485 = 16.7\%$, which is slightly above the percolation limit of $p_c \approx 14.5\%$ in the continuum model.[15] In the 8th cycle, f_m decreases to 8.4% ($M_{obs}/M_{FM} = 0.2938/3.485 = 8.4\%$). The values of f_m are 17.2% in the 1st cycle and 8.6% if we take $M_{FM} = 3.395 \mu_B$. As a consequence of the decrease of f_m, percolation is lost and so is the metallic character of the resistivity at low temperatures. Including a finite value for M_{AF} due to canting above 1.5 T could modify the actual value of f_m, but the decrease of the ferromagnetic phase fraction is still undisputable.

When the sample is field cooled under $H = 2$ T [main panel of Fig. 4(b)], the ferromagnetic phase fraction is 19.6% and it reduces to 14.2% ($\approx p_c$) in the 8th cycle when the sample becomes insulator. These results clearly suggest that the increase of resistivity is related to the decrease of the ferromagnetic phase fraction. Since f_m increases with lowering T below ~ 150 K in the 1st cycle, the effect of thermal cycling upon increase of ρ also decreases with T_S, lowering below 160 K.

At this moment a doubt could be raised: Is the decrease of M due to random freezing of moments of ferromagnetic clusters by local anisotropy fields instead of change in the ferromagnetic phase fraction? If cluster freezing is the dominant mechanism, the anisotropy energy is expected to increase in conjunction with the increase in resistivity and we can anticipate the maximum in the zero field cooled magnetization (ZFC) to shift up in the temperature with cycling.[16] To verify this point we carried out the ZFC-$M(T)$ in $H = 1$ mT and $H = 2$ T. Figure 5(a) shows $M(T)$ under $H = 1$ mT in the ZFC mode after cooling the sample in zero field from 250 K to 10 K each time. The data were taken over a smaller temperature range compared to Fig. 4(a) but it serves our purpose. In the first cycle, $M(T)$ increases smoothly from 10 K and exhibits a maximum around 57 K. However, in the second cycle $M(T)$ decreases dramatically in value the temperature range 20–110 K and in the next two cycles the change is rather small. The dramatic decrease of M value in the 2nd cycle is not expected in a conventional cluster or spin glass.[16] We do not observe the anticipated upward shift of the maximum; instead, the ZFC-M(T) curves in the second, third, and fourth cycles show a maximum at $T \approx 30$ K. Figure 5(b) shows $M(T)$ under $H = 2$ T in the ZFC mode. All the curves again exhibit a maximum at the same temperature ($T = 30$ K) which also allows us to conclude that cluster freezing is not the dominant mechanism in reducing the
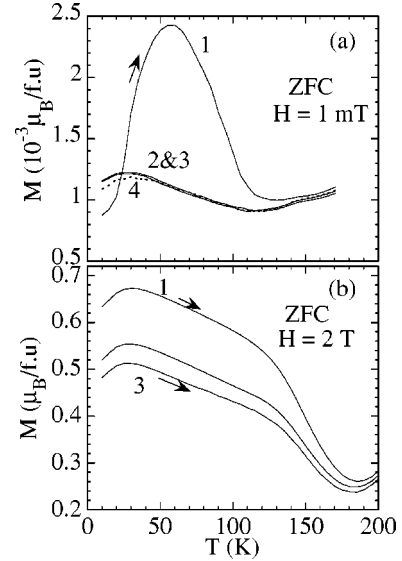

FIG. 5. $M(T)$ of $Pr_{0.5}Ca_{0.5}Mn_{0.985}Cr_{0.015}O_3$ under zero field cooled mode for (a) $H = 1$ mT and (b) $H = 2$ T.

value of the magnetization, but that the decrease in the ferromagnetic phase fraction is the possible origin.

What could be the mechanism which drives the diminution of the ferromagnetic phase? The ferromagnetic metallic (FMM) and the charge ordered insulating (COI) phases are expected to differ structurally because of the larger degree of Janh-Teller distortion in the latter phase and its absence in the former phase. Then, inhomogeneous strains exist in the interfacial regions. In a first order transition in which elastic interactions between the parent and the product phases are non-negligible (example martensitic transition[18]), growth of the product phase does not progress as a function of time as one would expect, but needs changes in the thermal energy. The rapid decrease in the magnetization between the first two cycles and the gradual decrease in the later cycles resemble the evolution of strain in the first few thermal cycles (known also as "training") in athermal martensitic materials.[19] In charge ordered phase, d_{Z^2} orbital ordering due to the Jahn-Teller distortion creates anisotropic strain. We observed changes neither in intensity nor in the value of the charge-orbital modulation vector **q** by electron microscopy at 92 K under thermal cycling (not shown here), however we cannot exclude possible changes in the interfacial regions. We also carried out an x-ray diffraction study at $T = 300$ K and at $T = 100$ K which is the lowest temperature limit in our x-ray instrument (Philips- X'pert) on a piece of a virgin sample and on a sample which has become an insulator after thermal cycling. We carried out the Rietveld analysis in *pbmn* settings. The results are presented in Tables I and II. Although we find changes in the structural parameters between the two samples, errors in the parameters (see the numbers within brackets) are too large to be reliable. It is possible that structural changes occur mostly in the interfacial regions between the ferromagnetic and the charge ordered phase which could not be detected in the present x-ray study due to smaller width of the interfacial regions. Millis *et al.*[17] showed that biaxial strain due to the Jahn-Teller distortion could lead to

TABLE I. Variation of lattice parameters and atomic positions of the virgin and the cycled $Pr_{0.5}Ca_{0.5}Mn_{0.985}Cr_{0.015}O_3$ samples in *Pbmn* settings. The number in the bracket indicates error.

			$T=300$ K		$T=100$ K	
			Virgin	Cycled	Virgin	Cycled
		$a=$	5.4048(7)	5.4076(4)	5.4304(14)	5.4324(10)
		$b=$	7.6059(8)	7.6075(7)	7.4977(9)	7.5004(8)
		$c=$	5.3932(7)	5.3954(4)	5.4250(12)	5.4268(9)
Pr/Ca	$4c{:}x,1/4,z$					
		x	0.0270(7)	0.0266(5)	0.0297(9)	0.0297(8)
		z	$-0.003(3)$	$-0.001(3)$	$-0.002(2)$	$-0.005(2)$
Mn/Cr	$4b{:}0,0,1/2$					
O(1)	$4c{:}x,1/4,z$					
		x	0.489(5)	0.490(4)	0.487(5)	0.485(5)
		z	0.065(9)	0.058(6)	0.052(7)	0.072(5)
O(2)	$8d{:}x,y,z$					
		x	0.299(5)	0.286(5)	0.281(9)	0.271(6)
		y	0.035(4)	0.040(3)	0.033(4)	0.036(3)
		z	$-0.283(7)$	$-0.287(5)$	$-0.289(7)$	$-0.293(5)$

localization of charges and decrease the Curie temperature. Then, a plausible explanation is that upon thermal cycling the Jahn-Teller distortion of $Mn^{3+}O_6$ octahedras in the interfacial regions increases; as a result the interfacial elastic energy increases which impedes the growth of the ferromagnetic phase during thermal cycling similar to the martensitic transition.[18] We do not think that granularity effects play any important role in our results since we find a systematics in the behavior of the thermal cycling effect with different x although all the compounds were prepared under identical conditions. Very recently, similar thermal cycling induced phenomena but less dramatic effect than our results was also reported in $Gd_5(Si_{1.95}Ge_{0.25})$.[20]

IV. CONCLUSIONS

In conclusion, we have shown that the insulator-metal transition in the phase separated $Pr_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ manganites is unstable with respect to thermal cycling. While the resistivity much above the I-M temperature is found to be unaffected, the resistivity close and below the I-M transition is strongly affected by repeated thermal cycling. Repeated thermal cycling is found to increase the low temperature resistivity and even destroys the metallic transition in $x=0.015$. The effect is strongly dependent on the composition and decreases with increasing x. We have shown that the ferromagnetic phase fraction decreases with repeated thermal cycling. Our x-ray and electron diffraction studies do not

TABLE II. Variation of bond distances and bond angles of the virgin and the cycled $Pr_{0.5}Ca_{0.5}Mn_{0.985}Cr_{0.015}O_3$ samples in *Pbmn* settings. The number in the bracket indicates error.

		$T=300$ K		$T=100$ K	
		Virgin	Cycled	Virgin	Cycled
Ca/Pr-	O(1)×1	2.37(5)	2.40(4)	2.45(4)	2.36(3)
	O(1)×1	2.52(3)	2.53(2)	2.50(3)	2.51(3)
	O(1)×1	2.93(3)	2.92(2)	2.96(3)	2.99(3)
	O(1)×1	3.04(5)	3.01(4)	2.99(4)	3.09(3)
	O(2)×2	2.35(3)	2.36(3)	2.40(4)	2.40(3)
	O(2)×2	2.64(3)	2.63(3)	2.63(3)	2.60(3)
	O(2)×2	2.67(3)	2.69(3)	2.63(4)	2.66(3)
	O(2)×2	3.19(3)	3.18(3)	3.14(4)	3.14(3)
Mn/Cr-	O(1)×2	1.93(1)	1.928(6)	1.897(6)	1.917(6)
	O(2)×2	1.89(3)	1.95(3)	1.92(4)	1.87(3)
	O(2)×2	2.01(3)	1.96(3)	1.98(4)	2.04(3)
	Manganese-oxygen-manganese angle				
Mn-	O(1)-Mn	158.8(1.4)	161(1)	162.4(1.2)	156.0(8)
Mn-	O(2)-Mn	155.7(1.8)	155.6(1.4)	158.4(2.1)	158.4(1.4)

show any clear evidence for change in structural parameters of the bulk, although changes in interfacial regions cannot be excluded. We suggest that increase of the elastic energy in the ferromagnetic-charge ordered interface might be the origin of the instability of the I-M transition. Contrary to the thermal cycling effect, resistivity at a given temperature is found to decrease slowly as a function of time. Further ex-

perimental and theoretical studies are necessary to clarify the origin of the observed effects.

ACKNOWLEDGMENTS

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