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Conversion of a glassy antiferromagnetic-insulating phase to an equilibrium ferromagnetic-metallic phase by devitrification and recrystallization in Al substituted $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

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Abstract

We show that $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ with 2.5% Al substitution and $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO) exhibit qualitatively similar and visibly anomalous $M-H$ curves at low temperature. Magnetic field causes a broad first order but irreversible antiferromagnetic (AF)–insulating (I) to ferromagnetic (FM)–metallic (M) transition in both and gives rise to a soft FM state. However, the low temperature equilibrium state of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ (PCMAO) is FM-M whereas that of LCMO is AF-I. In both systems the respective equilibrium phase coexists with the other phase with contrasting order, which is not in equilibrium, and the cooling field can tune the fractions of the coexisting phases. It is shown earlier that the coexisting FM-M phase behaves like ‘magnetic glass’ in LCMO. Here we show from specially designed measurement protocols that the AF-I phase of PCMAO has all the characteristics of magnetic glassy states. It devitrifies on heating and also recrystallizes to an equilibrium FM-M phase after annealing. This glass-like AF-I phase also shows a similar intriguing feature observed in FM-M magnetic glassy state of LCMO, that when the starting coexisting fraction of glass is larger, successive annealing results in a larger fraction of the equilibrium phase. This similarity between two manganite systems with contrasting magnetic orders of respective glassy and equilibrium phases points to a possible universality.

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

1. Introduction

The complexity of strongly correlated electronic systems has many intriguing manifestations in transition metal oxides [1], and perovskite manganites are amongst these [2]. The prototype charge ordered (CO) half-doped manganite $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ undergoes a transition to a CO insulating (I) state with antiferromagnetic (AF) order on lowering the temperature. Under application of large magnetic field this charge order melts into a charge liquid metallic (M) state with ferromagnetic (FM) order. Substitution in the Mn site causes an interesting effect on the CO and low temperature state [3]. It has been shown that minimal quench disorder in

the magnetic lattice of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ in the form of 2.5% substitution of Al in Mn sites weakens the so-called robust CO and ‘finite size clusters’ are formed [4]. It is shown that AF-I state of this system, $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ (PCMAO), can be converted to a FM-M state by moderate fields at low temperature [5]. However, the system does not get back to its original zero-field-cooled (ZFC) state (AF-I) when the field is withdrawn isothermally. This naturally brings up the question about the equilibrium phase; is the ZFC state (AF-I) the equilibrium phase or is the remnant state (FM-M) the equilibrium phase? Similar irreversibility in isothermal magnetization is observed in other half-doped manganites where has been proved that the equilibrium phase

at low temperature is AF-I [6, 7]. Significantly, it is revealed from specially designed high field measurement protocols that this minimal substitutional disorder radically changes the low temperature AF-I equilibrium phase in the parent compound to FM-M in PCMAO [5, 6]. Cooling and heating in an equal field (CHEF) shows that a fraction of the AF-I phase transforms to the FM-M phase with the decrease in temperature and the low temperature state shows coexisting FM-M and AF-I phases. However, a specially designed ‘cooling and heating in unequal fields’ (CHUF) protocol is used to clearly remove the ambiguity about the low temperature equilibrium phase.

While the AF-I and FM-M phases in half-doped manganites are separated by a first-order transition in the space of field (H) and temperature (T) control variables, the low temperature equilibrium phase is often masked by the glass-like arrest of the kinetics of the phase transformation. The arrested high temperature AF-I phase persists untransformed when PCMAO is cooled in zero field to low temperatures. Cooling in higher fields shows the AF-I to FM-M transformation with lowering temperature; the transition is hysteretic during warming. The fraction of the arrested AF-I phase can be tuned by cooling the sample in different fields (but at the same cooling rate), and this coexists with the transformed FM-M phase at low temperature [5, 6].

We present in this paper detailed measurements on PCMAO to show that the glass-like arrested AF-I state is similar to the ‘magnetic glass’ state recently reported in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO) [8], and can also be similarly devitrified and recrystallized. The interesting contrast is that in LCMO the arrested state has FM order and is metallic, whereas in PCMAO the arrested state has AF order and is insulating. In section 2, we shall give details of our sample and the measurement methodology. Results and discussions (section 3), start by depicting a qualitatively similar but clearly anomalous isothermal field cycling effect on the magnetization (M) of both PCMAO and LCMO. In section 3.1, we shall report magnetization at varying temperature in various fixed fields. We show that an AF-I to FM-M transformation, with hysteresis characteristic of a first-order transition, is observed for $H \geq 1$ T. Simultaneously, hysteresis characteristics of a first-order transition will be shown in resistivity measurements. In these measurements we follow the CHEF protocol. In section 3.2, we present magnetization measurements when we follow the CHUF protocol. A special case of this protocol is the commonly used zero-field-cooled (ZFC) protocol; our general version allows the heating field H_h to be smaller or larger than the cooling field H_c . Our measurements of magnetization as a function of temperature show topologically different features depending on the sign of $H_h - H_c$. We shall link this with our proposed phenomenology [9, 10]. We have recently reported that while the arrested glass-like FM-M state in LCMO devitrifies on heating, cooling after annealing causes better recrystallization to the AF-I state [8]. In section 3.3, we shall show similar results in PCMAO. The contrast with LCMO is that here the arrested state is AF-I and the recrystallized state is FM-M. We shall then show that, as in LCMO [11], successive annealing causes better recrystallization. Finally, we show in section 3.4, that if the starting glass-like AF-I fraction is

larger, then similar successive annealing produces a larger recrystallized equilibrium FM-M fraction. This apparently counterintuitive result has been reported earlier in LCMO [11], and we shall comment on possible implications of this general observation.

2. Experimental details

In this study we have used the same $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ sample as in [3–6]. The preparation and characterization details for this sample can be found in [3]. The $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ sample is the same as used in [8, 11]. The magnetization and resistivity measurements were performed using commercial setups [14 T physical property measurement system-vibrating sample magnetometer (PPMS-VSM), M/s. Quantum Design, USA]. All the temperature variations are made at a fixed rate of 1.5 K min^{-1} . This is relevant because the cooling rate dependence of glass-like arrest phenomena will not be invoked here.

3. Results and discussions

Figures 1(a) and (b) show the effect of magnetic field cycling on the magnetization of the PCMAO and LCMO samples, respectively, at 5 K after cooling in zero field. Both the samples show a field induced broad first-order transition from the AF to the FM state in moderate fields (>5.5 T for PCMAO and >8.5 T for LCMO) in the initial field-increasing cycle. As the field is increased towards the maximum available field of 14 T, the magnetization approaches the spin-aligned value of $3.5 \mu_B/\text{Mn}$ expected for these manganites around half-doping. However, the field-decreasing cycle does not show the reverse first-order FM to AF transition, nor does the next field-increasing cycle shows the AF to FM transition observed in the original state. It is rather interesting that the subsequent field cycling portrays $M-H$ as resembling the soft FM state for both samples. It may be noted that the initial increase in magnetization of LCMO immediately above zero field is because of the untransformed FM phase which got arrested while cooling in zero field [8]. Thus, both the samples show a qualitatively similar anomaly in isothermal magnetization.

3.1. Cooling and heating in equal field (CHEF)

To probe the above mentioned anomalous state we measure the magnetization of PCMAO while cooling and heating in an equal field. Figure 2(a) shows the magnetization in different fields following the CHEF protocol. This clearly shows a broad first-order AF to FM transition with decrease in temperature. This is in clear contrast to the observations made in LCMO, where FM to AF transition is observed during cooling [8, 12]. However, even in an 8 T field, a fully saturated moment value is not achieved much below the closure of the thermal hysteresis. This indicates that the AF phase is not fully transformed to the FM phase at the lowest temperature. This can be clearly observed in the inset of figure 2(a), where along with the $M-H$ curves of 5 K, the magnetization values at 5 K in different

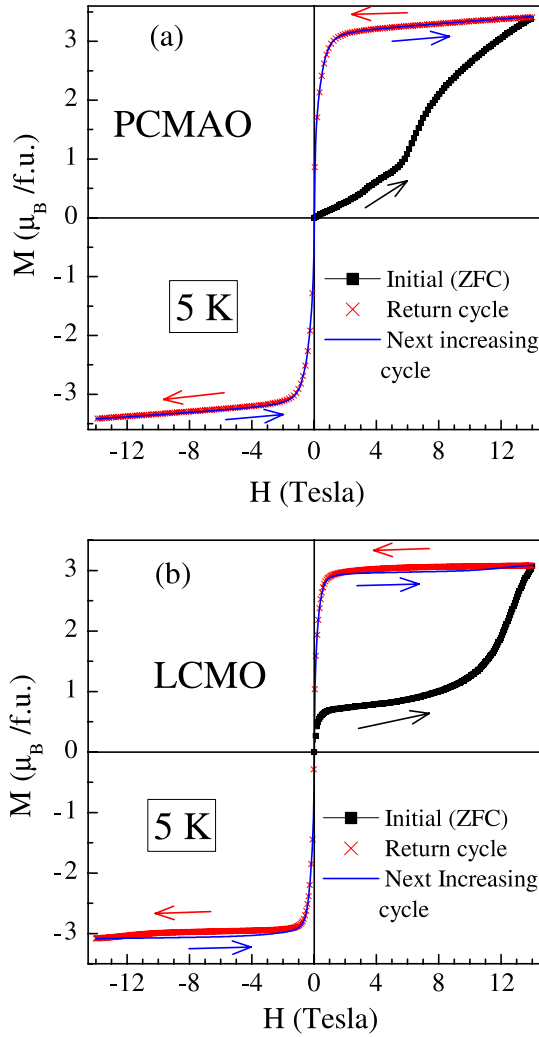


Figure 1. $M-H$ curves of PCMAO and LCMO at 5 K after cooling the samples from 320 K in zero field. (a) Initial field-increasing cycle of PCMAO shows a linear increase in magnetization at lower fields for the AF state. Then it undergoes a broad field induced transition to the FM state at higher fields and approaches the spin-aligned moment value at 14 T. However, the field-decreasing cycle does not show the reverse transition to the AF state, indicating an anomaly in the field induced first-order transition. With the decrease in H , magnetization decreases to zero, resembling a soft FM state. This is evident in the subsequent field cycling which shows a hysteresis loop without any observable opening. (b) $M-H$ of LCMO following the same measurement protocol as in (a). The initial increase in magnetization just above zero field is because of the presence of a fraction of the soft FM phase which became arrested during cooling in zero field. The remaining AF phase fraction undergoes a field induced transition to the FM state; thereafter it shows soft magnetic behavior in subsequent field cycles akin to PCMAO. In both cases, the ZFC AF-I state cannot be retrieved after the field induced transition to the FM-M state, unless the sample is warmed above the superheating temperature.

fields after cooling in the same fields are plotted. All the field-cooled magnetizations in cooling and measuring fields between 1 and 8 T show moment values below the return envelope curve, indicating the existence of different fractions of the untransformed AF phase. This fraction decreases in higher cooling fields and a fully transformed FM phase is obtained when the system is cooled in $H \geq 10$ T. It is interesting to note

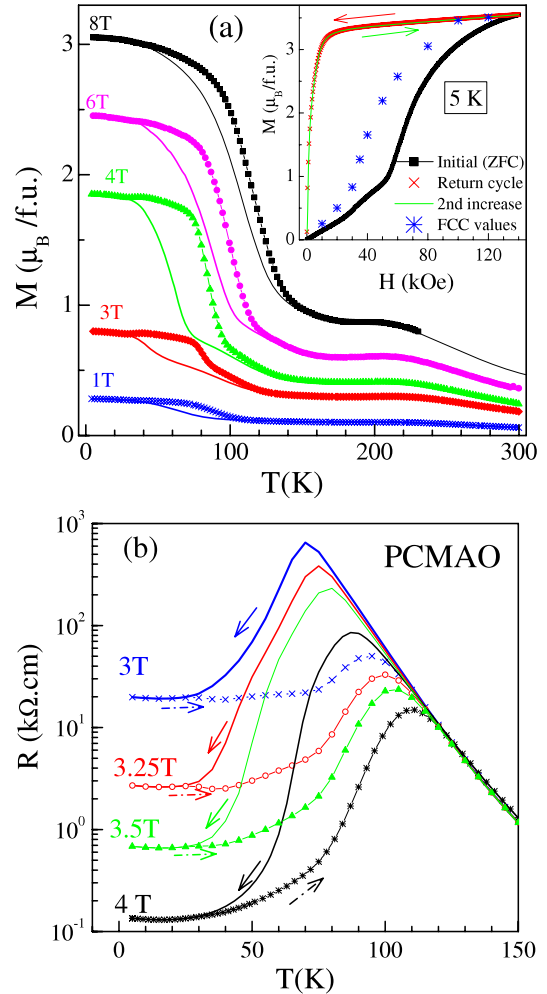


Figure 2. Temperature induced broad first-order transition from the AF-I to the FM-M state of PCMAO in different fields. (a) The AF to FM transition does not appear to have transformed the complete sample to the FM state even much below the closure of thermal hysteresis, indicating an incomplete first-order transformation process. The magnetization values at lowest temperature are much less than the values expected for such a soft FM state. This is clearly brought out in the inset of (a) where the magnetization values in different fields at 5 K after cooling in the same fields are plotted along with $M-H$. For $H < 10$ T these values fall between initial and return curves, indicating the coexistence of AF and FM phases at the same field and temperature. (b) The thermal hysteresis of resistivity in different fields from the I to the M state which are associated with the AF and FM phases, respectively, for PCMAO.

that cooling in fields lower than the field required to cause the first-order field induced transition at 5 K (≈ 5.5 T) also converts a fraction of the AF phase, resulting in moment values higher than that of the initial field-increasing state.

Figure 2(b) show the resistivity of PCMAO in different fields measured following the CHEF protocol. These show a broad first-order insulator to metal transition with decrease in temperature. However, an anomaly similar to the magnetization one is also observed in resistivity in isothermal field variation at 5 K, which was shown recently in [5]. Hence, similar to LCMO, coexisting phases with different fractions of AF-I and FM-M phases can be created at low temperature in PCMAO [5, 6], one may be in equilibrium and

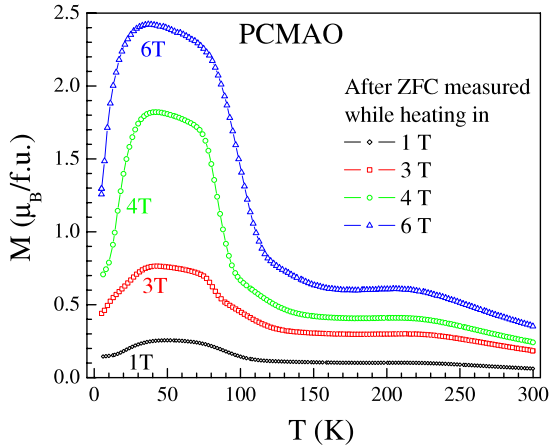


Figure 3. Magnetization of PCMAO in different fields while warming after cooling in zero field. The sharp increase from lowest temperature signifies devitrification of the arrested AF-I phase to the equilibrium FM-M phase. With a further increase in temperature, magnetization shows a sharp fall arising from the reverse conversion of the FM-M to the AF-I phase on approaching the superheating limit. Thus, heating in a field higher than the cooling field (zero in this case) gives rise to two sharp changes with opposite signs, one at low temperature because of devitrification to the low temperature equilibrium phase and another at higher temperature resulting from first-order transition to the high temperature equilibrium phase having contrasting order.

the other in the ‘magnetic glassy’ state. The above mentioned measurements following the CHEF protocol show that the AF-I phase partially transforms to FM-M on cooling, which is the converse of what is observed in LCMO. However, CHEF does not bring out the glass-like arrested character of the coexisting AF-I phase fraction.

3.2. Cooling and heating in unequal fields (CHUF)

In this section we show that the nature of coexisting AF-I and FM-M phases at low temperature in PCMAO can be identified by the uncommon measurement protocol CHUF. As mentioned earlier, heating in finite fields of the zero-field-cooled (ZFC) state is a special case of CHUF, and data are shown in figure 3. After cooling in zero field, a different field is applied each time while measuring the magnetization during heating. All these curves show an initial increase with the increase in temperature, and the increase is sharper for higher fields. CHEF protocols have not shown any increase at these low temperatures for the corresponding measurement fields (figure 2(a)). Moreover, the magnetization value at 5 K is much less compared than the value achieved when cooled in the same measurement fields (figure 2(a)). It is shown in figure 2(a) that cooling and measuring in a field < 10 T renders a fraction of the AF-I phase untransformed at 5 K. Figure 3 shows a much larger fraction of untransformed AF-I phase when the magnetization is measured in the corresponding fields after ZFC, consistent with the inset of figure 2(a). The sharp increase in magnetization of this state with the increase in temperature clearly indicates the rapid transformation of the untransformed AF-I phase fraction to the FM-M phase. Such

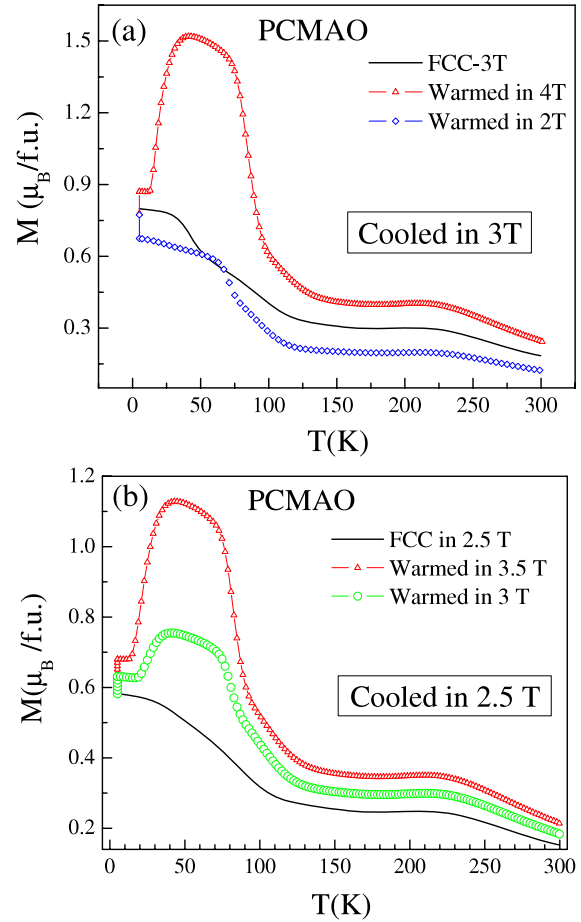


Figure 4. Magnetization following the CHUF protocol (defined in the text) after cooling in fixed field but warming in unequal fields. (a) Shows magnetization in 2 and 4 T while warming after cooling in 3 T along with the 3 T cooling run. When the cooling field (H_c) is lower than the heating field (H_h), magnetization shows two sharp changes of opposite signs arising from devitrification followed by reverse conversion, whereas when $H_c > H_h$ the change associated with devitrification is absent. (b) Shows magnetization in 3 and 3.5 T while warming after cooling in 2.5 T along with the 2.5 T cooling run. Here, both the warming fields (H_h) are higher than H_c and as a result the magnetization in both cases shows two sharp but opposite changes. The sharp increase in magnetization associated with devitrification for the lower warming field (3 T) starts at a higher temperature than the 3.5 T curve because the devitrification starts on approaching the kinetic arrest band which, for this case (FM-M ground state), moves to higher temperature with decreasing field (see [5, 6]).

rapid transformation to the low temperature equilibrium phase when thermal energy is imparted to the system is akin to devitrification, which is evidence of a glassy state [13]. Though this state shows transformation to the FM-M state with time (not shown here), a more visual and informative (as discussed below) manifestation of devitrification on the magnetization is shown following the CHUF protocol in figures 4 and 5.

In figure 4 we show CHUF measurements of magnetization, comparing data for the same value of H_c but different values of H_h . We have data for various values of H_c , but show only representative data for (a) $H_c = 3$ T and (b) $H_c = 2.5$ T. For all H_c de-arrest of AF-I to FM-M is observed only when $H_h > H_c$. A similar dependence of CHUF magnetization on

the sign of $H_h - H_c$ was used in [6] to distinguish the equilibrium phase from the glass-like arrested coexisting phase in different manganites around half-doping, highlighting the novelty of CHUF. The sharp rise in magnetization at low temperature resulting from de-arrest of the AF-I phase is also observed for ZFC measurements. The arrested AF-I fraction is fixed by H_c , but as shown in figure 4(b) the extent of de-arrest (or rise in magnetization) is greater when H_h is higher. This feature is observed for all values of H_c , including the data for $H_c = 0$ in figure 3. This feature is consistent with T_K , the temperature for glass-like arrest, falling as H rises [5, 6].

It was shown earlier for variety of systems that broad H and T induced first-order transitions can be represented by quasi-continuum of supercooling (T^*) lines, corresponding to spatial distribution of regions in the sample of the dimension of the correlation length, forming T^* bands in $H-T$ space [9, 10, 14]. Consequently, $H-T$ dependent glass-like arrest of kinetics was also represented by the T_K band in $H-T$ space [9, 10, 14]. The CHUF magnetization is related to the sign of the slopes of the T^* and T_K bands in $H-T$ space for this case. Significantly, it was proposed that the nature of correlation between the T^* and T_K bands can be revealed from the CHUF measurements [9]. We now discuss such measurements for PCMAO.

In figure 5 we show two representative examples of CHUF with (a) $H_h = 3$ T and (b) $H_h = 4$ T. The features outlined below have also been observed for various other values of H_h . We again find that de-arrest is observed whenever $H_c < H_h$, but not when $H_c > H_h$, corresponding to an equilibrium FM-M phase at low temperature. We note that as $H_h - H_c$ becomes smaller in magnitude, de-arrest is initiated at higher temperature. This was also observed in La-Pr-Ca-Mn-O [10] and corresponds to the T^* and T_K bands being anti-correlated, i.e. regions with above-average T^* have below-average T_K . It is rather intriguing that such anti-correlation was shown to be universal for all other systems where ‘magnetic glassy’ states are identified [10, 14, 15]. Evidence of the anti-correlation is clear in figure 5, where the CHUF measurements show that for fixed H_h , de-arrest is initiated at higher temperature for higher H_c . This is exactly as predicted by the phenomenology for a FM equilibrium and AF arrested phase (see figure 3(c) of [10]). We stress that the CHUF measurements not only allow us to identify both the existence and magnetic order of the ‘magnetic glassy’ state but go deeper to probe correlation between T^* and T_K without making recourse to the time domain [16].

3.3. Recrystallization of the glass-like AF-I phase by single and successive annealing

Unambiguous and rather visual evidence of the coexisting AF-I ‘magnetic glassy’ state in PCMAO was given in the previous section from devitrification. In this section, we show that a fraction of this magnetic glass can be recrystallized by single annealing and a larger fraction by successive annealing to the FM-M phase, analogous to the conventional structural glass [13]. Figure 6 shows this recrystallization of the AF-I phase fraction to FM-M by single annealing through magnetization measurement. Cooling the sample from room

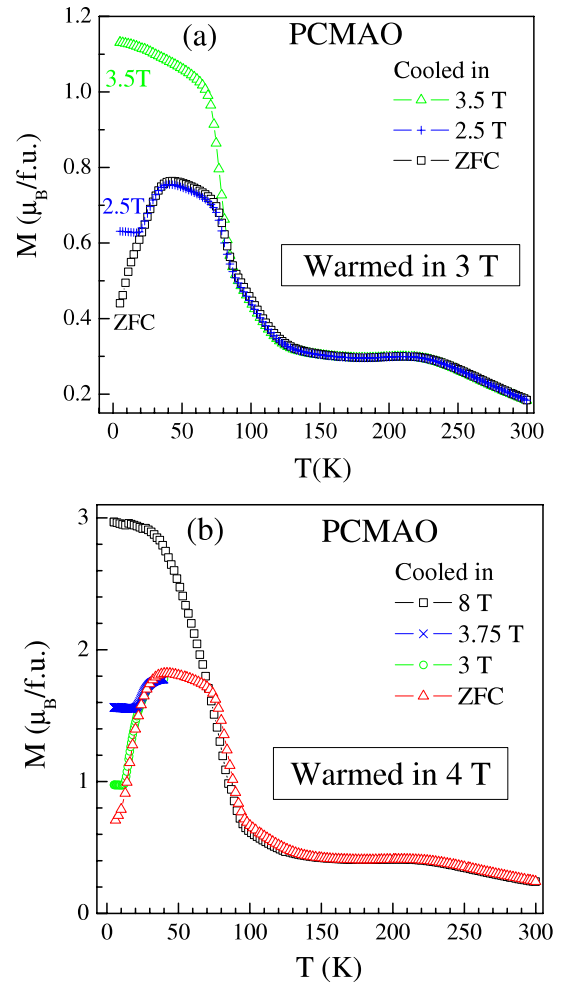


Figure 5. Magnetization while warming following the CHUF protocol where H_c is varied but H_h is kept fixed. (a) Cooling fields are 0, 2.5 and 3.5 T and the warming field (H_h) is 3 T. It is clear that when $H_c < H_h$ (in case of $H_c = 0$ and 2.5 T) there are two sharp changes whereas for $H_c = 3.5$ T there is only one sharp change at higher temperature because of reverse transformation to the AF-I state. (b) In this case H_h is fixed at 4 T after cooling in 0, 3, 3.75 and 8 T. The behavior is consistent with the sign of $H_c - H_h$. Devitrification starts at lower temperature for $H_c = 3$ T than for $H_c = 3.75$ T.

temperature in 2 T results in larger fraction of AF-I phase at 5 K, a fraction of which gets devitrified to the FM-M phase indicated by a sharp increase in magnetization while warming after isothermally changing the field to 5 T at 5 K. However, instead of heating all the way up to room temperature, the sample is heated only up to 60 K and cooled back again without changing the field. This cooling from 60 K results in a higher magnetization value at 5 K, more than the value found after cooling the sample from room temperature in 5 T (FCC). Thus a fraction of residual AF-I phase is recrystallized to FM-M phase upon annealing to 60 K, producing a larger magnetization in the same field (5 T) and temperature (5 K) than the corresponding FCC value. Similar recrystallization by single annealing can be observed in the inset of figure 6 when the initial cooling from room temperature as well as all the subsequent temperature cyclings are performed in a fixed field of 5 T. It is obvious from this

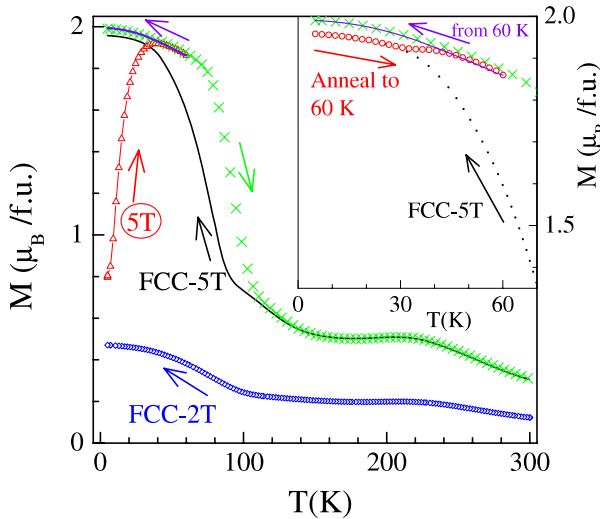


Figure 6. Recrystallization of the FM-M phase in PCMAO after single annealing at 60 K is shown through magnetization measurements. When the sample is cooled in 2 T the magnetization at 5 K is small because of the presence of a large fraction of arrested AF-I phase. After isothermally changing the field at 5 K to 5 T the magnetization is measured during warming. The sharp increase indicates devitrification of a fraction of the arrested AF-I phase to the FM-M phase. After warming to 60 K the sample is cooled again. This second cooling after annealing to 60 K results in higher magnetization at 5 K in 5 T compared to its value when the sample is directly cooled in 5 T from 320 K. In the inset we show this clearly by cooling and annealing in the same field. For the inset, magnetization is measured while cooling in 5 T, then while warming from 5 to 60 K and again while cooling to 5 K followed by warming all the way. It is clearly seen that the second cooling after annealing to 60 K produces larger magnetization at 5 K than its value after initial cooling. This confirms recrystallization of the FM-M phase fraction after single annealing at 60 K.

figure that there is significant increase in magnetization after annealing to 60 K compared to its value after the initial cooling.

Now we show more effective recrystallization of the AF-I magnetic glassy fraction by successive annealing through both resistivity and magnetization measurements. Figure 7 shows the large resistivity of PCMAO at 5 K when cooled and measured in a field of 2.1 T. Thereafter the resistivity is measured in the same field of 2.1 T while heating and cooling, each time annealing at progressively higher temperatures. The resistivity of only a few such temperature cycles is shown for clarity. It is evident that the resistivity at 5 K decreases after each annealing at successively higher temperatures up to the annealing temperature of 60 K, indicating recrystallization of arrested AF-I phase to FM-M phase. However, the increase in resistivity after annealing at 80 K occurs because of the reverse transformation of the FM-M phase fraction to AF-I phase on approaching the superheating spinodal of first-order transformation. This trend continues for other temperatures >80 K (not shown here). Qualitatively similar effects of recrystallization by successive annealing are observed in resistivity measurements in many other fixed cooling and annealing fields. This is the converse of our report on LCMO where the glassy arrested phase is FM-M and the equilibrium phase is AF-I.

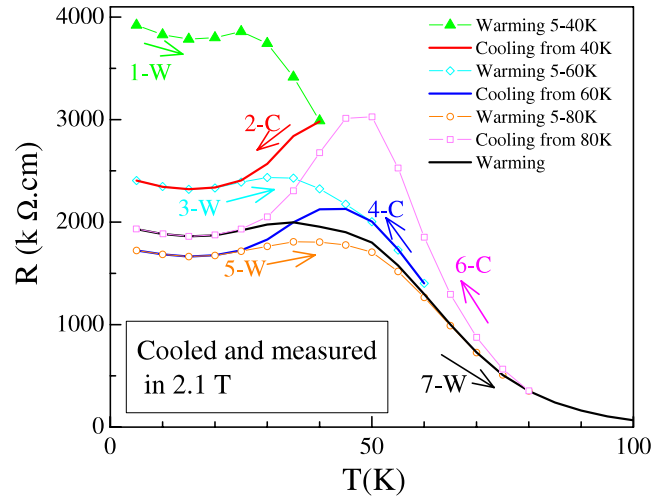


Figure 7. Recrystallization of FM-M phase from glass-like arrested AF-I phase in PCMAO during successive annealings at progressively higher temperatures through resistivity measurement in 2.1 T. Resistivity shows a large value at 5 K after cooling in 2.1 T, arising from larger fraction of AF-I phase. This value of resistivity at 5 K decreases substantially after annealing to 40 K. Further decrease in this value occurs after annealing to 60 K. Thereafter, this value shows an increasing trend when annealed to 80 K or higher because of reverse transformation to the AF-I phase and also rules out any artifact related to irreversible change in the sample. Successive warming (W) and cooling (C) cycles are sequentially numbered along with the direction of the respective temperature excursion (denoted by W or C).

Figure 8 shows recrystallization by successive annealing through measurement of magnetization while cooling and annealing in a fixed field of 5 T, each time traversing to progressively higher temperatures. It is shown in figure 2(a) that a fraction of the high temperature AF-I phase remains untransformed at 5 K when cooled in 5 T. Now, if this glass-like arrested state is subjected to successive annealing then recrystallization to the equilibrium FM-M phase takes place, showing a concomitant increase in magnetization at 5 K. It needs to be reiterated that such recrystallization in LCMO occurs from glass-like arrested FM-M to equilibrium AF-I phase, whereas in the present case of PCMAO the phases appear in reverse order.

3.4. More glass gives better crystal

In this section we give evidence of an intriguing but unequivocal experimental observation that is rather counterintuitive and significant. We show that when the starting fraction of the glassy phase is higher, successive annealing in the same field produces larger fraction of equilibrium (crystal) phase at low temperature. This is demonstrated in figure 9 by measuring magnetization at fixed temperature (5 K) after each annealing in the fixed field (5 T) at successively higher temperatures. Two initial states with different fractions of arrested AF-I phases are produced at 5 K by cooling in 2 and 5 T. Then after isothermally changing the field to 5 T for the 2 T cooled state, magnetization is measured at 5 K for both these states after successive annealings at progressively higher temperatures without

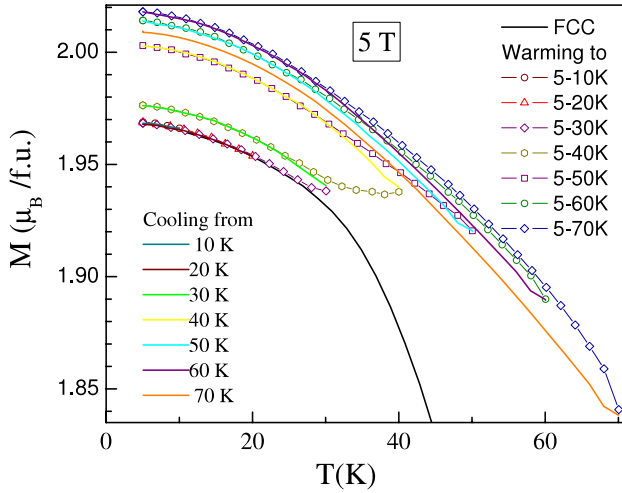


Figure 8. Recrystallization of FM-M phase from glass-like arrested AF-I phase in PCMAO during successive annealing at progressively higher temperatures (increasing in steps of 10 K) through magnetization measurement in 5 T. Magnetization is measured during cooling in 5 T, producing a smaller value at 5 K. Then cooling to 5 K after annealing at 10 and 20 K does not produce a noticeable change. Thereafter, the magnetization at 5 K shows consecutively higher values with successive annealings up to 60 K. Then after annealing at 70 K or higher the magnetization at 5 K starts coming down because of reverse transformation.

changing the field. In figure 9 magnetization at 5 K in 5 T is plotted as a function of annealing temperatures. As shown in figure 2(a), the 2 T cooled state has larger fraction of AF-I phase at 5 K compared to the 5 T cooled state. When the field is isothermally changed to 5 T, this state gives a much lower magnetization value at 5 K (see inset of figure 9) compared to the 5 T cooled state. The magnetization value of this state at 5 K remains lower than the 5 T cooled state even after successive annealings up to 20 K (see inset of figure 9). After next annealing to 30 K, the magnetization of both states becomes almost equal. Significantly, annealing to subsequent higher temperatures (up to 70 K) shows a drastic effect: the 2 T cooled state has a higher magnetization than the 5 T cooled state in the same measurement field and temperature. Thus, when the starting fraction of glass-like arrested AF-I phase is higher, successive annealing produces a larger fraction of crystal-like equilibrium FM-M phase for the same measurement conditions. A similar intriguing effect has been observed in LCMO for different measurement fields as well as for different initial fractions of glass [11, 17], though in that case the glassy phase is FM-M and here the glassy phase is AF-I. A close look at the data in figure 5(b) in the range $70 \text{ K} < T < 130 \text{ K}$ also indicates that more glass gives better crystal.

4. Conclusions

We conclude that all the characteristic features of the FM-M magnetic glassy state of LCMO also exist for the kinetically arrested AF-I phase in PCMAO. We bring out the similarities as well as contrasts between the two manganites around half-doping, giving the highlights of the present study

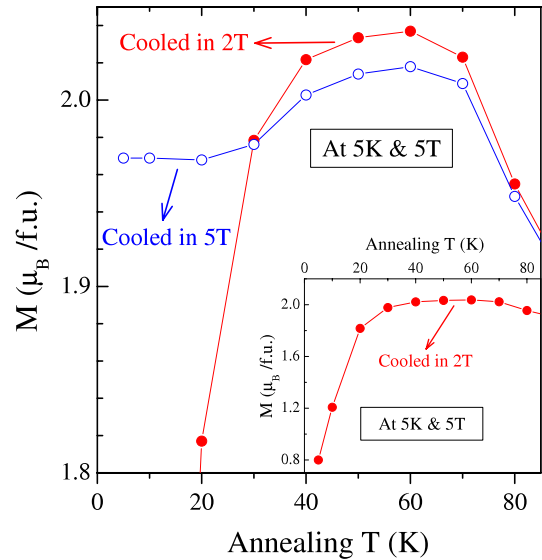


Figure 9. Evidence of a larger fraction of glass-like AF-I phase producing a larger fraction of equilibrium (crystal-like) FM-M phase by successive annealing. Magnetization values measured in 5 T at 5 K after initial cooling in 5 T and after successively annealing at progressively higher temperatures in the same measurement field (5 T) are plotted as a function of respective annealing temperatures. The glass-like AF-I phase fraction in the 5 T cooled state progressively recrystallizes to FM-M phase during successive annealings up to 60 K. Thereafter, it starts decreasing because of reverse conversion. The 2 T cooled state has a larger fraction of arrested AF-I phase at 5 K, resulting in much smaller magnetization (as shown in the inset) when the field is isothermally changed to 5 T. Even after annealing this state in the same measurement field (5 T) to 10 and 20 K the magnetization at 5 K in 5 T is much smaller than the corresponding values for the 5 T cooled state. However, after annealing to 30 K the magnetization at 5 K steeply rises to become equal and thereafter it shows a significant overshoot from the corresponding values of the 5 T cooled state with each annealing up to 60 K. This clearly shows that the presence of a larger fraction of glass-like AF-I phase triggers conversion of a larger fraction to the FM-M phase.

below. (i) PCMAO and LCMO show qualitatively similar but anomalous isothermal $M-H$ behaviors at low temperature. Both show a field induced broad first-order transition from the AF-I to the FM-M state which is not reversible. The resulting FM-M state is a soft ferromagnet without observable hysteresis. (ii) PCMAO shows temperature induced first-order transition from the AF-I to the FM-M state with decrease in temperature but opposite transition from the FM-M to the AF-I state is observed for LCMO, indicating the contrasting nature of the equilibrium phase. However, in both systems the complementary order coexists with the equilibrium phase fraction at the lowest temperature. (iii) A specially designed measurement protocol, CHUF, can unravel the nature of the coexisting non-equilibrium phase, which is found to be glass-like. Significantly, CHUF allows us to probe deeper into the phenomenon of ‘magnetic glass’ and brings out an anti-correlation between superheating and glass transition temperatures of different regions of the sample. (iv) This glass-like AF-I state in PCMAO resembles the conventional glass. Moreover, similar to the magnetic glass of LCMO (having

magnetic order of the opposite type), it devitrifies on heating, recrystallizes after annealing and does so more effectively by successive annealing. (v) The most interesting as well as intriguing observation of this study is that a larger fraction of equilibrium phase can be recrystallized when the starting equilibrium fraction is smaller in the coexisting phase. In other words, more glass makes better crystal both in PCMAO and LCMO.

Thus, there appears to be a universality in the magnetic glassy state irrespective of its magnetic order or electron transport properties. This needs to be explored for other systems and with other experimental techniques. It also needs to be checked whether this conclusion of ‘more glass gives more crystal’ is valid for structural glasses. We must record that traversal of unconventional (H , T) paths is experimentally much easier than traversal of similar (P , T) paths that would be required for structural glasses. This is because H is varied at the sample without a medium, which does not complicate independent variation of the two control parameters. We thus expect systems like those studied here to shed more light on the physics of glasses.

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