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2010 J. Phys.: Condens. Matter 22 032101

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Field dependence of temperature induced irreversible transformations of magnetic phases in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ crystalline oxide

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Received 25 September 2009, in final form 16 November 2009

Published 16 December 2009

Online at stacks.iop.org/JPhysCM/22/032101

Abstract

Glass-like arrest has recently been reported in various magnetic materials. As in structural glasses, the kinetics of a first order transformation is arrested while retaining the higher entropy phase as a non-ergodic state. We show visual mesoscopic evidence of the irreversible transformation of the arrested antiferromagnetic–insulating phase in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ to its equilibrium ferromagnetic–metallic phase with an isothermal increase of magnetic field, similar to its iso-field transformation on warming. The magnetic field dependence of the non-equilibrium to equilibrium transformation temperature is shown to be governed by Le Chatelier’s principle.

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

1. Introduction

The understanding of glasses remains a challenge in spite of being the subject matter of active research for more than 30 years. Glasses form when kinetics is arrested below a temperature T_g , preserving the high temperature structure while avoiding the first order liquid–crystal transformation. Vitrification is considered as a dynamic singularity upon supercooling below T_g [1]. Devitrification to the crystalline state on warming is taken as the evidence of the glassy state [2]. The critical cooling rate required for vitrification of metallic glasses has been shown to fall sharply as the ratio of T_g to the melting temperature T_m rises [2, 3]; the suppression of T_m with increasing pressure has been used to vitrify monoatomic germanium at achievable cooling rates [4].

The magnetic properties of many colossal magnetoresistance (CMR) manganites exhibit non-equilibrium ‘glassy’ behavior [5–10]. Since the phases on either side of the

transition have a long-range structure as well as magnetic order, this behavior does not correspond to a magnetic metglass [11] or spin glass [12]. This new type of glassy behavior, reported in materials ranging across intermetallics [12–15] and CMR manganites [6–8, 10, 16–18, 20], has been termed as magnetic glass [7, 10, 12–14, 16, 17]. Here a first order magnetic transition is inhibited by a lack of kinetics, and the high temperature higher entropy phase persists as glass-like arrested states (GLAS). This arrested state is the high- T phase that exists at low- T , where another state with competing order has a lower free energy. Being the high- T equilibrium state, this arrested state has higher entropy and must be ‘disordered’ as compared to the low- T equilibrium state. The disorder causing this higher entropy is not always apparent, reminding us of solid ^3He , of solid ^4He , and of their mixtures. It has been conjectured [7] that the dynamics of this type of magnetic glass may not be fundamentally different from that of structural glasses. The question whether

these systems exhibit a glass transition with new degrees of freedom has recently also been addressed [10]. In fact, the similar dynamics in these GLAS is reflected in the decay of the arrested state following the Kohlrausch–Williams–Watts form as one approaches an arrest temperature T_K that is analogous to the glass transition temperature T_g [13, 14], and also in the arrested state showing an irreversible transformation to the equilibrium state on warming [6, 14, 16, 18] that is analogous to the devitrification seen in structural metallic glasses on warming [2]. Further, these magnetic glasses have an excess specific heat that varies linearly with T , as in conventional glasses, including orientational glasses [17]. For these reasons, we shall follow terms recently introduced in literature [6–8, 10, 12–18], and refer to the higher entropy structurally ordered arrested magnetic states as ‘magnetic glass’ and their irreversible transformation on warming to another but lower entropy equilibrium state as ‘devitrification’.

The glass-like behavior observed at low temperatures is considered to be one of the most intriguing features of phase separated manganites [7, 8]. Depending on the system, the GLAS can be antiferromagnetic [6–8, 14] or ferromagnetic [6, 13, 15, 16]. The half-doped colossal magnetoresistance (CMR) manganites have an important advantage over other materials because the conductivity changes drastically along with magnetic order across the transition. While a decrease of global magnetization in the sample can be interpreted as either a reduction of moment in the ferromagnetic metallic (FM–M) phase, or as part transformation of FM–M to an antiferromagnetic insulator (AF–I), a simultaneous measurement of conductivity provided a clear choice between the two alternatives because of the orders of magnitude resistivity changes associated with the metal (M) to insulator (I) transition in the latter case. A visual demonstration of both these types of changes, i.e. a change in the phase fraction [7] as well as a change in the global magnetization, can be captured by mesoscopic measurements with a magnetic force microscope (MFM).

It has been shown in recent literature [6, 8, 10] that while an equilibrium phase coexistence is due to quenched impurities that lead to the spread of the local transition temperatures (where local means over length scales of the order of the correlation length), and a consequent rounding of the first order phase transition (FOPT), the static phase coexistence persisting to lower temperature without a change in phase fraction is due to glass-like arrest of the transformation kinetics (recent work [10] identifies a possible kinetics that is frozen at T_g). $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Mn}_{0.975}\text{Al}_{0.025}\text{O}_3$ (PCMAO) is one of the extensively studied members of this class of magnetic glasses, whose GLAS is an AF–I, while the low temperature equilibrium state is a FM–M [6, 18]. The fraction of the glass-like AF–I phase at a given H increases by making the cooling field H_C smaller¹. The AF–I phase obtained as a homogeneous state on cooling PCMAO in $H = 0$, shows all the characteristics of a glassy state including devitrification. Just as devitrification of metallic glass involves a sudden change in density, devitrification of

the magnetic glass involves a sudden change in magnetization. A specially designed ‘cooling and heating in unequal fields’ (CHUF) protocol has been used to show that devitrification occurs whenever this sample is warmed in a magnetic field (H_w) that is higher than the field (H_C) it was cooled in; a reentrant AF–I to FM–M to AF–I transition is seen on heating as devitrification at T_g is followed by the first order transition at T^{**} analogous to melting at T_m [18]. Here we show that while T^{**} rises with increasing H (as expected), T_g falls with rising H . This implies that devitrification can be caused on raising H isothermally, since the T_g – H line will be crossed from the low- T (AF–I magnetic glass) to high- T (FM–M equilibrium) state. This would follow Le Chatelier’s principle (à la pressure increase resulting in a crossover to the high density state); except that the celebrated principle describes a system in equilibrium, whereas devitrification is clearly a non-equilibrium process. This conclusion is supported by mesoscopic MFM measurements showing that devitrification takes place with the isothermal increase of H , similar to devitrification observed on heating.

2. Experimental details

In this study we have used the same PCMAO sample as in previous studies [6, 17–19]. The preparation and characterization details for this sample can be found in [19]. The magnetization measurements were performed using a 14 T physical property measurement system-vibrating sample magnetometer (PPMS-VSM), Quantum Design, USA. For MFM measurements the sample was polished to a mirror finished surface by repeated grinding and polishing. Magnetic imaging was carried out using a low temperature high field magnetic force microscope from NanoMagnetics Instruments, UK along with 9 T superconducting magnet system from American Magnetics, USA. NANOSENSORS™ PPP-MFMR cantilevers with resonance frequency ≈ 70 kHz are used in the present study. The microscope utilizes the noncontact mode for magnetic as well as topographic scans. In this mode the cantilever is tuned to its resonance frequency when it is in free condition or well away from the surface. The cantilever is brought closer to the sample surface while monitoring the change in its resonance amplitude and frequency. During the forward scan the oscillation amplitude (i.e. root mean square of amplitude V_{rms}) is maintained constant by varying the tip height, thus giving topographic information. The reverse scan is used for magnetic imaging where the cantilever is lifted by 50 nm (called lift off) and follows the topography measured during the forward scan. The change in amplitude (V_{rms}) during this scan gives the magnetic profile of the surface.

3. Results and discussion

In figure 1 we show measurements of M versus T following the CHUF protocol. Cooling the sample from 300 to 5 K in a cooling field $H_C = 3.25$ T results in coexisting phases with the AF–I phase fraction being about 70%. We now study the devitrification behavior of this magnetic glass as it is heated in different fields, in an attempt to see how T_g depends on H . The

¹ The fraction of the glass-like phase can of course be controlled, in a limited range, by varying the cooling rate. But here the fraction is controlled while keeping the cooling rate fixed.

sample is warmed in a field $H_w = 4$ T and the devitrification to the FM–M phase is seen through a sharp rise in M that starts at 16 K and terminates at ≈ 40 K, with the mid-point (T_g at 4 T) being at ≈ 20 K. The reentrant transition, corresponding to melting, is seen by a sharp fall in M , with the mid-point of the transition (T^{**} at 4 T) being at 84 K. We again cool the sample from 300 to 5 K in a cooling field $H_C = 3.25$ T to obtain the same initial state with the AF-I phase fraction being about 70% [6] and now warm from 5 K after increasing the field to $H_w = 5$ T. The devitrification to the FM–M phase is again seen through a sharp rise in M , that now starts at 9 K and terminates at about 35 K, with the mid-point (T_g at 5 T) being about 15 K. The mid-point of the reentrant transition, corresponding to melting, (T^{**} at 5 T) is 90 K. We again cool the sample from 300 K to 5 K in a cooling field $H_C = 3.25$ T and now warm from 5 K after increasing the field to $H_w = 6$ T. The devitrification to the FM–M phase is again seen through a sharp rise in M , that now starts at 5 K itself and terminates at ≈ 30 K, with the mid-point (T_g at 6 T) being at ≈ 10 K. The mid-point of the reentrant transition, corresponding to melting, (T^{**} at 6 T) is 98 K. We see that T^{**} rises with increasing field so that an isothermal increase of H would, in a specific range of T , convert the AF-I state to FM–M. This is consistent with the qualitative condition imposed by Le Chatelier’s principle on a system in equilibrium; the value of dT^{**}/dH should of course be consistent with the Clausius–Clapeyron relation, since this is a first order transition. We now note that T_g at 4 T is 20 K, while the mid-point of T_g at 6 T is 10 K. T_g thus falls with increasing field, and an isothermal increase of H would, in a certain range of T , convert the glass-like AF-I phase to the equilibrium FM–M phase by devitrification. This is consistent with the qualitative condition imposed by Le Chatelier’s principle in that increasing H takes the system to a state with higher M . Except that the glass-like AF-I phase is not a system in equilibrium, and devitrification is not an equilibrium process.

Devitrification under an isothermal increase of H is not just a conjecture, and we present MFM data to support this. In figure 2 we show MFM pictures of the reentrant AF-I to FM–M to AF-I transformation with increasing T . The sample is cooled from 300 to 5 K in $H = 0$, and the field is raised to 7 T. We observe coexistence of antiferromagnetic (light color) and ferromagnetic (dark color) regions, at the micron level, as has been inferred under the ZFC condition [6]. We now raise T and note an increase in the FM fraction at $T = 40$ K, as shown in the histogram in the bottom panel. Since the response of cantilever changes with temperature, we have shown histograms of normalized V_{rms} (V_{norm}). The reentrant melting to the antiferromagnetic phase is seen starting at 90 K, and we have an almost homogeneous AF-I phase at 150 K. This devitrification followed by ‘melting’ with warming is as expected for any structural glass.

We now show in figure 3 the isothermal behavior of the glass. The sample is cooled to 6 K in zero field, and H is then varied isothermally. At $H = 1$ T, the sample is mostly antiferromagnetic, and a major fraction of the ferromagnetic phase is seen at $H = 6$ T. We now reduce H to 1 T (bottom panel), and find that there is no reverse transformation during

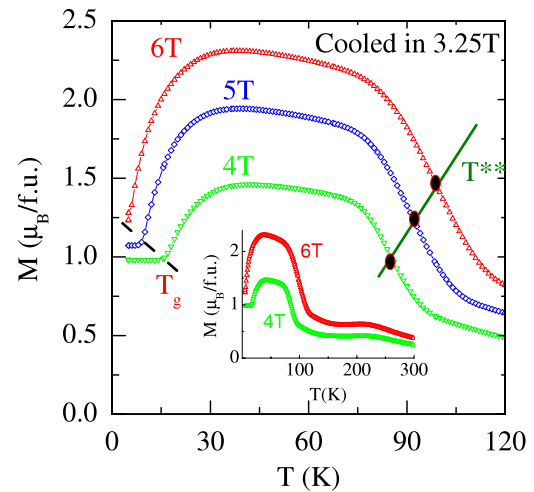


Figure 1. Magnetization (M) as a function of temperature during warming in the presence of the labeled magnetic field. For each of these measurements the sample is cooled in the presence of 3.25 T to 5 K and the magnetic field changed to the labeled field isothermally. Devitrification at low temperature and the reverse transformation to the AF-I state is highlighted. The dashed and solid lines shows T_g and T^{**} for these curves. See the text for details. The inset shows the magnetization while warming in 4 and 6 T after cooling in 3.25 T for the complete temperature range.

the field reduction. The magnetic profile of the sample at 1 T is identical to that of the 6 T image, which shows a much higher ferromagnetic phase compared to the first 1 T image. Then H is raised to 7 T with a visible increase in the ferromagnetic region; reducing H to 1 T again causes no reverse transformation. We then raise H to 9 T (our experimental limit) with a further visible increase in the ferromagnetic region; reducing H to 1 T again causes no reverse transformation.

We thus show that increasing H isothermally at 6 K causes an irreversible conversion from the antiferromagnetic to ferromagnetic phase, as expected in the process of devitrification. We performed magnetization measurements under the same protocol of cooling in zero field to 6 K and then varying H isothermally as above (figure 4). In the initial field increasing cycle, the first order field induced AF-I to FM–M transition starts around 5.3 T. After reaching the target field (H_t) of 6 T the field is reduced to 1 T, but this 1 T value is much higher than the initial 1 T value. It is important to note that in the next field, increasing the cycle to 7 T, the magnetization follows the same path up to 6 T. Again the 1 T value after returning from H_t of 7 T gives higher values than previously. A similar feature is repeated for H_t of 9 T. Each return from progressively higher H_t shows higher values at 1 T, there is no back conversion and the field increasing path overlaps with the previous field decreasing path up to the previous H_t . These clearly indicate that the field induced transformed FM–M phase fraction does not undergo reverse transformation with the reduction of field, which is visually demonstrated in the maps of the bottom panel of figure 3. The minor decrease in magnetization between its value at H_t and the return cycle is because of the global decrease in magnetization. This is also reflected in the maps of figure 3, the shades of the bottom panel

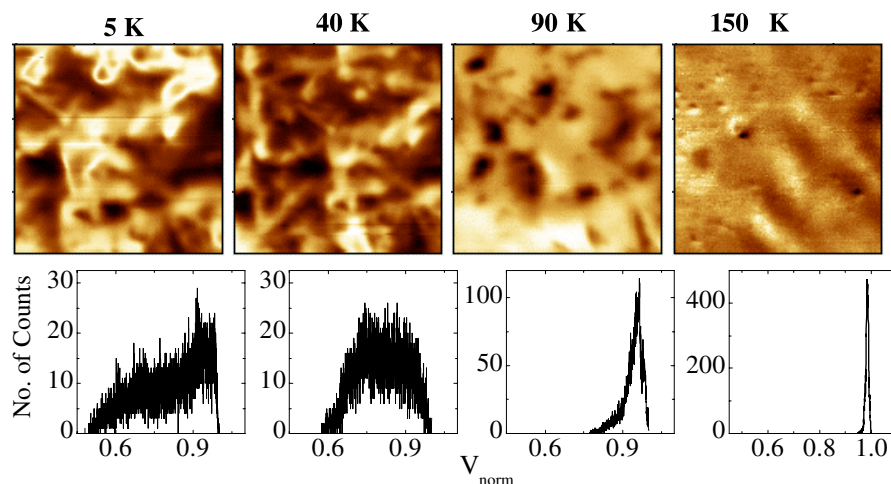


Figure 2. MFM images of PCMAO in $H = 7$ T taken during warming after the sample is cooled to 5 K in zero field. The magnetic field is applied isothermally at 5 K. The dark color corresponds to ferromagnetic regions. The reentrant transformation from the AF-I to the FM-M state (devitrification to FM as T is raised from 5 to 40 K) to the AF-I state (‘melting’ of FM to AF as T is raised from 40 to 90 K) is observed. The distribution of normalized amplitude variation V_{norm} (bottom panel) indicates coexisting FM and AF regions, while at 150 K the sample is AF and homogeneous. The frame size of each MFM scan is $17 \mu\text{m} \times 17 \mu\text{m}$.

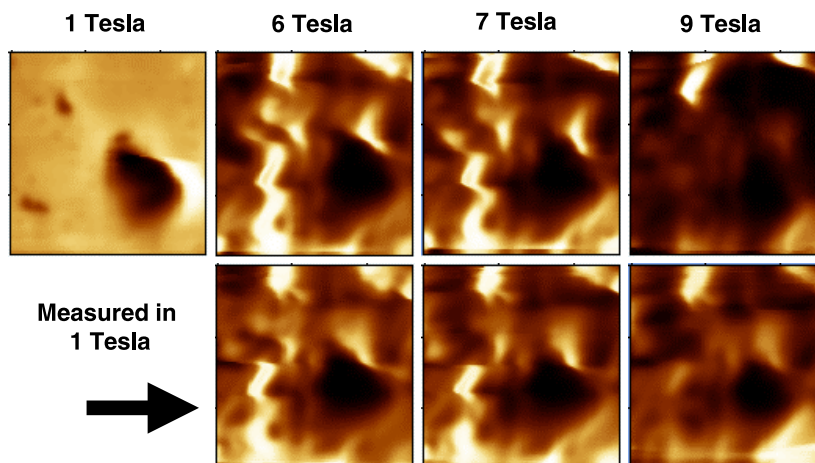


Figure 3. MFM images of PCMAO with increasing magnetic field (top row) after the sample is cooled to 6 K in zero field. Dark patches correspond to ferromagnetic regions. Magnetic images were also taken at 1 T (bottom row) after reducing the magnetic field (isothermally at 6 K) from that shown in the top row. The magnetic profiles remain unchanged on reducing the magnetic field to 1 T, showing an irreversible isothermal transformation from AF-I to FM-M as expected in devitrification. The frame size of each MFM scan is $17 \mu\text{m} \times 17 \mu\text{m}$.

are lighter than the top because of the global decrease in the magnetization without any change in the phase fractions. Thus the results shown in figure 4 are consistent with the MFM data of figure 3.

We have obtained data similar to that in figure 1 following the CHUF protocol for $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (NSMO), where the glassy phase is FM-M and coexists with the equilibrium AF-I phase [20]. In this system the FM-M glassy phase devitrifies to the equilibrium AF-I phase on warming for a measuring field lower than the cooling field showing a reentrant transition. For the same measurement field, this reentrant transition shifts to a lower temperature for larger cooling fields i.e. T_g rises and T^{**} falls with increasing H in NSMO. This corresponds to isothermal devitrification of the non-equilibrium ferromagnetic phase to the equilibrium antiferromagnetic phase with decreasing H . This is again

consistent with the qualitative condition imposed by Le Chatelier’s principle, in that decreasing H takes the system to a state with lower M . Except that the glass-like FM-M phase is not a system in equilibrium, and devitrification is not an equilibrium process.

4. Conclusions

We have shown that the AF-I magnetic glass phase devitrifies with increasing H , and the FM-M magnetic glass devitrifies with decreasing H . This behavior is consistent with the magnetization of the magnetic glass being smaller or larger than that of the equilibrium or ‘crystal’ state. Metallic glasses also show devitrification, followed by melting, on heating; a reentrant behavior reminiscent of what is observed in magnetic

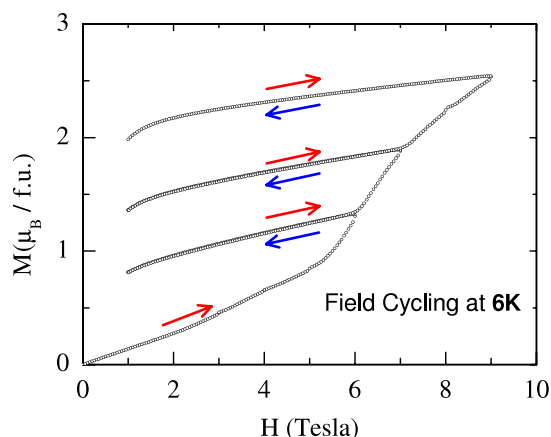


Figure 4. Magnetization (M) versus magnetic field (H) at 6 K corresponding to MFM images shown in figure 3. The irreversible isothermal transformation (devitrification) from the AF-I to the FM-M state is highlighted.

glasses under a suitable CHUF protocol. Devitrification observed in the metallic glasses involves a sudden change in density, just as devitrification here involves a sudden change in magnetization. It would be interesting to pursue pressure induced devitrification studies in metallic glasses to see if the glasses that have lower density (higher density) than the crystalline state devitrify with increasing (decreasing) pressure.

Acknowledgment

The Department of Science and Technology (DST), Government of India is acknowledged for funding the 14 T PPMS-VSM at CSR, Indore.

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