

Enhancement of equilibrium fraction in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ by recrystallization

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 255245

(<http://iopscience.iop.org/0953-8984/20/25/255245>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 13:16

Please note that [terms and conditions apply](#).

Enhancement of equilibrium fraction in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ by recrystallization

A Banerjee, Kranti Kumar and P Chaddah

UGC-DAE Consortium for Scientific Research (CSR), University Campus, Khandwa Road, Indore, 452017, India

E-mail: alok@csr.ernet.in

Received 31 January 2008, in final form 21 April 2008

Published 27 May 2008

Online at stacks.iop.org/JPhysCM/20/255245

Abstract

The nature of the coexisting ferromagnetic–metallic (FMM) and antiferromagnetic–insulating (AFI) phases in a $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ sample is explored through magnetization and resistivity studies. Like many first-order magnetic transitions, in this case also the FMM–AFI transformation is interrupted by glass-like arrest of kinetics. As a result, a fraction of the high-temperature FMM phase persists in a glassy state to the lowest temperature. We show that this glassy FMM phase devitrifies to equilibrium AFI phase on heating. Significantly, it can be ‘recrystallized’ to AFI state by annealing and more easily by successive annealing, presumably by heterogeneous nucleation. We show that the recrystallization is easier when the starting glass fraction is larger.

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

1. Introduction

Structural glasses and spin-glass are formed when the high-temperature disordered state persists in a regime where its free energy is no longer the minimum [1–4]. Disorder is not however the defining property of a glass, with amorphous silicon being the well cited example [2]. Recently, glass-like arrest of kinetics across first-order magnetic transition has been reported in materials ranging across intermetallics [5–8], shape-memory alloys [9], magnetocaloric materials [10, 11], colossal magnetoresistance (CMR) manganites [12–17] etc. Similar to the structural glass, in these systems also, kinetics of the first-order transformation is arrested while preserving the high-temperature phase as a non-ergodic state. This state is unusual because it has long-range magnetic order as well as long-range structural order. The kinetic arrest is reflected in the decay rate of the supercooled state following Kohlrausch–Williams–Watts form as one approaches the glass transition temperature (T_g) [5, 10] and the arrested state shows devitrification on warming [11, 14, 15]. The decay time of a structural glass diverges as the temperature approaches T_g . In contrast, the supercooled metastable state decays faster as temperature is lowered towards T^* because its local minimum in free energy becomes shallower and vanishes at T^* [18, 19]. Because of this, the decay rate increases with the decrease in temperature for a supercooled state whereas the decay rate

decreases with the decrease in T for the glassy state [12, 17]. The magnetic glass state is thus different from a metastable supercooled state.

The first-order transition temperature (T_C) in real systems will have a distribution, because of the intrinsic disorder, for regions having dimension of the order of the correlation length [20]. Consequently, the superheating (T^{**}) and the supercooling (T^*) limits also have a distribution, and the resulting broad hysteretic transitions have been observed [21, 22]. This naturally implies that the arrest of kinetics leading to formation of glassy phase for the respective regions would also occur over a broader section in the control variable space (like H – T space) [23, 24]. These broadened bands result in interesting features depending on how one traverses the (H , T) space of control variables [8, 11–16, 24].

In this paper, we build upon the ideas introduced in the papers cited above and introduce new ideas through our studies on a manganite around half doping, namely $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO). This is similar to the sample where Loudon *et al* have shown a first-order transformation from high- T ferromagnetic to low- T antiferromagnetic phase [25], with a coexistence of ferromagnetic regions at low T , below the closure of hysteresis. We show that the AFI state is in equilibrium at low T and the FMM phase fraction exists as kinetically arrested glassy or non-ergodic state, based on magnetization (M) and resistivity (R) measurements similar to those reported

earlier [15, 16]. Further, on annealing, this glassy FMM phase fraction ‘crystallizes’ to equilibrium AFI phase, similar to glass ceramics [2]. Successive annealing converts a larger fraction of the glassy FMM phase of LCMO to the AFI state. The most significant as well as intriguing result of this study is the observation that a much larger fraction of the AFI state forms when the starting glass fraction (FMM) is larger. This is true for both single and successive annealing. This implies that ‘crystallization’ from glass is more efficient when the starting fraction of glass is larger.

2. Sample preparation and characterization

The polycrystalline LCMO sample has been prepared through a chemical route known as the ‘pyrophoric method’. High purity ($\geq 99.9\%$) La_2O_3 , CaCO_3 and $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ are taken in stoichiometric quantities as starting materials. These materials are dissolved in aqueous nitric acid and the resulting solutions are mixed together with triethanolamine (TEA). The complex solution is heated to dehydrate and decompose leaving behind organic-based, black, fluffy precursor powder. This dried mass is then ground to fine powder, pelletized and calcined at 1000°C for 3 h in oxygen atmosphere. The powder x-ray diffraction (XRD) is carried out using an 18 kW Rigaku Rotaflex RTC 300 RC diffractometer with $\text{Cu K}\alpha$ radiation. Rietveld profile refinement of the XRD pattern confirms that the sample is in a single phase without any detectable impurity and crystallizes in orthorhombic structure with the *pnma* space group. It is known that by varying preparation conditions, different samples with nominal composition of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ can be prepared having different fractions of FMM phase at low temperature [26]. For this study we choose one which is close to that used by Loudon *et al* [25]; however, we would like to emphasize that the exact details of the sample may not be the most important factor for the present study. The resistivity and magnetic measurements are performed using commercial set-ups (14Tesla-PPMS-VSM, M/s. Quantum Design, USA).

3. Results and discussion

3.1. Glass-like kinetic arrest of FMM phase

Non-ergodicity in the sample is demonstrated in figure 1. Each time, the sample is cooled from 320 to 5 K in different H and then M is measured while changing the field isothermally from H to $-H$ (figure 1(a)). Higher cooling field renders a larger fraction of ferromagnetic phase which remains frozen at 5 K even when the H is reduced to zero, as shown by distinct magnetization in the negative field cycles, which is a mirror image of the initial field cycle. This implies that different fractions of frozen ferromagnetic phase remain invariant when the field is reduced to zero for each case. When the same measurement is repeated at 25 K, as shown in figure 1(b), there is partial devitrification of the glassy FMM phase while reducing the field to zero. This is evident from the negative field cycles showing lower magnetization than the starting values. The reduction is larger for the higher

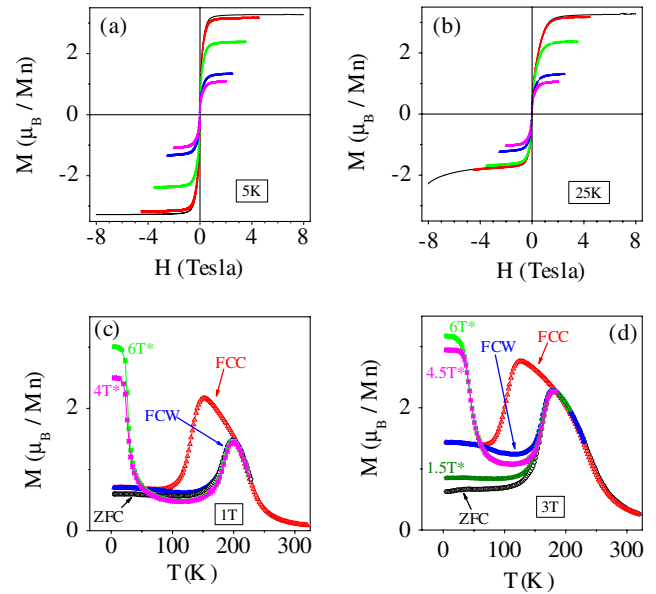


Figure 1. Evidence of glassy FMM phase fraction through magnetization of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. (a) The sample is cooled from 320 K in different $H = 2, 2.5, 3.5, 4.5$ and 8 T and M versus H is measured at 5 K while isothermally changing the H from $+H$ to $-H$. (b) M versus H at 25 K after following the same cooling protocol as panel (a). (c) M versus T measured in 1 T field. FCC and FCW magnetizations are measured while cooling and warming in 1 T. For the ZFC path, the sample is cooled in zero field. Again the sample is cooled from 320 K in 4 T or 6 T and the field is isothermally changed to 1 T at 5 K for $M-T$ while warming, marked in the figure as $4T^*$ and $6T^*$ respectively. (d) $M-T$ in 3 T. FCC and FCW are measured while cooling and warming in 3 T; ZFC is after cooling in zero field. Again the sample is cooled from 320 K in 1.5, 4.5 and 6 T and the field is isothermally changed to 3 T for $M-T$ while warming, marked in the figure as $1.5T^*$, $4.5T^*$ and $6T^*$ respectively.

cooling field because of the nature of the kinetic arrest band as discussed earlier [12, 24], which we briefly touch upon in the next paragraph. Thus figure 1(a) shows that cooling in different fields can control the fraction of glass-like arrested state; moreover, this fraction remains unchanged when the field is withdrawn at 5 K. The nature of this arrested phase is probed through $M-T$ measurements in 1 T field following different protocols as shown in figure 1(c). The disorder-broadened first-order transition from FMM to AFI phase with reducing temperature is evident from the hysteresis between field-cooled cooling (FCC) and field-cooled warming (FCW) paths. However, similar to [25], a sizable magnetization at 5 K, much below the closure of hysteresis, suggests the persistence of a fraction of ferromagnetic phase. Even after zero-field cooling (ZFC) there is substantial magnetization. This clearly indicates that the FMM to AFI transition is arrested and remains incomplete (even in zero field) at low T . After cooling the sample in 4 and 6 T, H is isothermally changed to the measurement H of 1 T at 5 K in both cases. Significantly larger but different magnetizations are now observed at the same H and T (1 T and 5 K), indicating non-ergodicity arising from additional glass-like arrested FMM phase. On warming, these states devitrify and the system approaches the equilibrium AFI

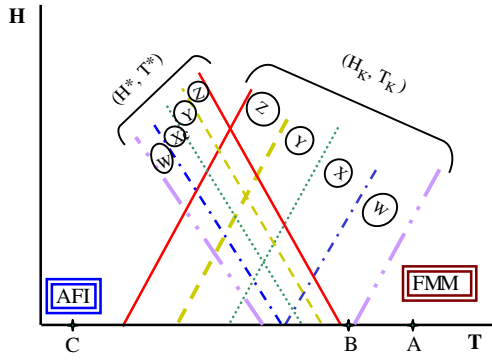


Figure 2. The heuristic H - T diagram for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The high- T phase is FMM and the low- T phase is AFI. The FMM phase can be supercooled to the (H^*, T^*) band. To represent the broad H - T induced first-order transition, only four regions (W, X, Y and Z) of the sample are shown in this schematic diagram. The glass-like arrest of kinetics will occur at the (H_K, T_K) band. Anticorrelation between supercooling and kinetic arrest is assumed (see [10, 12, 24] for details). Points A, B and C are as referred to in the text.

phase as shown by a rapid fall in M . Figure 1(d) shows similar measurements in 3 T after cooling in different H including zero field along with the FCC and FCW branches for 3 T. It may be noted that the magnetization evolves differently for the cases where the cooling H is larger than the measuring H from the cases where the cooling H is smaller than the measuring H . While the larger fraction of FMM phase accrued during cooling in H higher than the measurement H devitrifies on heating, no devitrification is evident in the presence of measurement H if the cooling fields are smaller (i.e. 0 and 1.5 T cases in figure 1(d)). This also indicates that the low- T equilibrium state is AFI, akin to the recent observations made in other half-doped manganites [15, 16].

To acquire semiquantitative understanding about the observations of figure 1 from the heuristic H - T phase diagram proposed for similar systems [24], we redraw it for the present case in figure 2. The supercooling (or superheating) line in the H - T space, across which the transformation takes place, is broadened by disorder into a band formed by a quasi-continuum of lines representing various regions (of dimension of the order of correlation length) of the sample. The sign of its slope reflects that the FMM phase will exist over a larger temperature range in higher fields. While cooling, if the system crosses this band unhindered, then it will convert to equilibrium AFI phase at low temperature. However, in the present system, the glass-like arrest of the transformation is depicted by a quasi-continuum of lines, forming the (H_K, T_K) band. The sign of the slope of the (H_K, T_K) band is consistent with the observation that when an increase in temperature causes devitrification to the AFI state (figures 1(c) and (d)) then isothermal devitrification must be observed on lowering the field as shown in figure 1(b). As the sample is cooled in zero H towards point A, we have a homogeneous FMM phase even though it is metastable. At point A, the entire sample is above the supercooling spinodal and no homogeneous nucleation takes place. Since regions corresponding to the W-band get kinetically arrested at point B, before there is

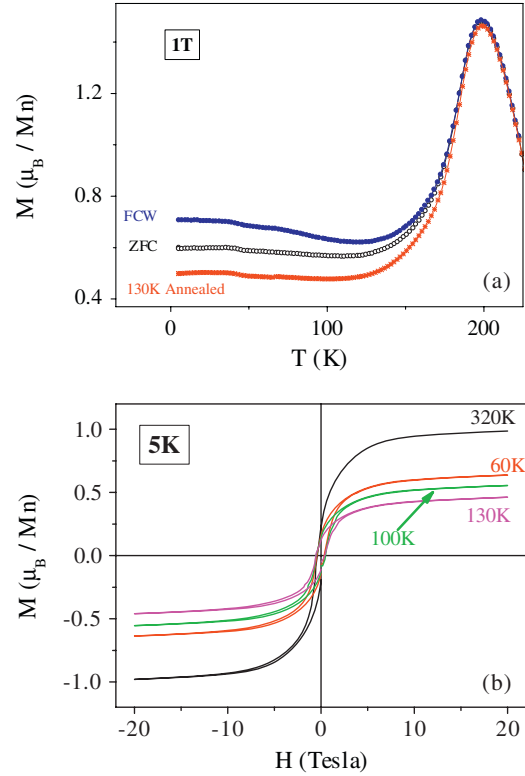


Figure 3. Effect of annealing and successive annealing on the magnetization of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. (a) M - T while warming in 1 T after cooling in zero field and 1 T. Again after cooling in 1 T the sample is annealed at 130 K and M - T is measured after cooling back to 5 K. (b) After cooling the sample in 2 T from 320 to 5 K the M - H is measured cycling the field between +2 and -2 T. Then the sample is annealed at progressively higher temperatures and M - H is measured at 5 K after cooling back from each annealing temperature as marked in the figure.

any homogeneous nucleation, these regions remain FMM at the lowest temperature of point C. But regions corresponding to bands X, Y and Z have been converted to AFI at this point C since their respective spinodal T^* is higher than their corresponding T_K . We now warm the sample to point B. We retain X, Y and Z in AFI phase, but W is kinetically arrested. We now warm toward point A. The W-band is no longer kinetically arrested; it is above its supercooling spinodal; but it is sitting in an environment where many nuclei of AFI phase exist corresponding to bands X, Y and Z. There is now a possibility of the FMM phase of band W undergoing heterogeneous nucleation and converting to the AFI phase. A closer scrutiny of the data on the present system will also justify an anticorrelation between the (H^*, T^*) and (H_K, T_K) band, which was proposed earlier [24] and experimentally verified for a variety of systems [8, 11, 12, 16].

3.2. Enhancement of equilibrium phase fraction by annealing

Now we show in figure 3, the conversion of the glassy FMM phase to the equilibrium AFI phase through the magnetization measurement. Figure 3(a) shows M - T in 1 T while warming from 5 K. After cooling in 1 T, the FCW path starts with a magnetization value of about $0.71 \mu_B/\text{Mn}$ at 5 K, whereas

after cooling in zero H the ZFC path has a starting value of about $0.6 \mu_B/\text{Mn}$. However, much smaller M of about $0.5 \mu_B/\text{Mn}$ can be achieved when the sample is cooled to 5 K in 1 T and then warmed to 130 K and cooled back to 5 K in 1 T. While warming, this 130 K annealed state evolves distinctly from the FCW or ZFC paths and finally merges with them on approaching the superheating limit around 200 K. The effect of successive annealing is shown in figure 3(b) through the $M-H$ measurements at 5 K after initially cooling in 2 T from 320 K. After initial cooling to 5 K, the field is cycled from 2 to -2 T at 5 K. Then the sample is warmed to 60 K in zero field and cooled back to 5 K in zero field, where $M-H$ is measured between ± 2 T. Annealing at 60 K has not only substantially reduced the glassy FMM phase fraction, the magnetization value in 1 T is even less than the ZFC value of $0.6 \mu_B/\text{Mn}$ at 5 K in 1 T. The sample is then successively annealed at higher temperatures in zero field, and each time $M-H$ is measured after cooling to 5 K in zero field, showing lower fraction of FMM phase. This way, after annealing to 130 K the magnetization at 5 K in 1 T is reduced to about $0.43 \mu_B/\text{Mn}$, which is lower than the $0.5 \mu_B/\text{Mn}$ achieved after a single annealing at 130 K (figure 3(a)). It was proposed earlier that the AFI phase ‘crystallizes’ from high-temperature FMM phase through the ‘nucleation and growth’ process [25]. During the initial cooling in 2 T, the ‘homogeneous nucleation’ process is dominant because there is no AFI seed in the sample [27]. During annealing the existing AFI phase provides seeds for heterogeneous nucleation leading to additional ‘recrystallization’. It is possible to achieve even more ‘recrystallization’ of the residual glassy FMM phase to AFI state by successive annealing [2]. It may be noted here that annealing in temperatures higher than 150 K results in the opposite effect because of back-conversion to FMM phase.

One intriguing feature of this glassy magnetic state is that it is easier to ‘recrystallize’ the glass when its starting fraction is larger. It has already been shown in figure 3(a) that annealing the 1 T cooled state to 130 K produces lower magnetization than the zero-field-cooled state. Figure 4 shows that a larger fraction converts to AFI phase when the starting FMM fraction is larger at 5 K. It is shown in figure 1(c) that a larger fraction of FMM phase can be created at 5 K if cooled in 6 T, and figure 4(a) shows that if this 6 T cooled state is annealed to 130 K then it produces a larger fraction of AFI phase and lower magnetization in 1 T at 5 K, which is even lower than the 1 T cooled state annealed to 130 K. Yet, larger conversion to AFI state can be achieved when the 6 T cooled state is subjected to successive annealing at progressively higher temperature. After cooling in 6 T to 5 K the field is reduced to zero and the sample is subjected to a temperature cycling between 5 K and T_H , where T_H starts from 60 K and each time it is increased by 10 K to go up to 130 K. Much lower magnetization is measured at 5 K in 1 T after this temperature cycle, which evolves distinctly on warming and merges with all others on approaching the superheating spinodal. This half-doped manganite is expected to have the spin-aligned value of $3.5 \mu_B/\text{Mn}$ accompanied by metallic conductivity [25]. The observed variation in magnetization at 5 K from 0.6 to

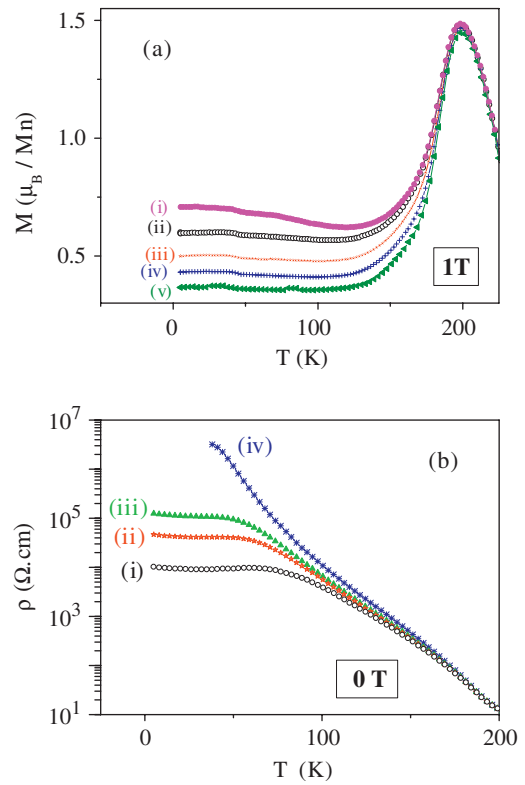


Figure 4. Effect of starting glass fraction on the ‘recrystallization’ of AFI phase in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. (a) $M-T$ while warming in 1 T. The sample is prepared at 5 K through (i) cooling in 1 T, (ii) cooling in zero field, (iii) cooling in 1 T and annealing once at 130 K, (iv) cooling in 6 T and annealing once at 130 K in zero field, (v) cooling in 6 T and after reducing the field to zero at 5 K annealing successively to 130 K as described in text. (b) $R-T$ in zero field while warming. The sample is prepared at 5 K through (i) cooling in zero field, (ii) cooling in zero field and annealing once at 140 K, (iii) cooling in 1 T and after reducing H to zero at 5 K annealing once at 140 K, (iv) cooling in 6 T and after reducing H to zero at 5 K annealing once at 140 K.

$0.37 \mu_B/\text{Mn}$ can be attributed to a variation of frozen FMM phase fraction from about 17% to 11%, which is close to the percolation threshold for electrical conductivity. Hence, around this FMM phase fraction, resistivity changes can be more drastic, which is vividly demonstrated in figure 4(b) by a colossal change in resistivity measured in zero field while warming from 5 K. The lower resistivity measured while warming from 5 K after cooling in zero field increases many-fold if the sample is annealed at 140 K. The resistivity increases further when the sample is cooled to 5 K in 1 T and then annealed to 140 K after reducing the field isothermally to zero at 5 K. Yet, orders of magnitude increase in resistivity is observed after cooling in 6 T and then reducing the field isothermally to zero at 5 K followed by an annealing at 140 K. The increase in resistivity is so gigantic that it exceeds the measurement range of the instrument until the sample is heated above 38 K. Successive annealing produces much larger resistivity for each case (not shown in the figure for clarity). Contrary to an earlier report of thermal cycling on a manganite sample [28], the observed changes are reversible and can be reproduced once the superheating limit is crossed or the sample

is heated to about 250 K. There is no permanent change in the sample, which is also evident from the fact that the successive annealing increases the resistivity at 5 K up to the annealing temperature of 150 K, and above this it decreases [29]. The observation of better conversion to AFI state when the starting fraction of glassy FMM phase is greater is rather intriguing.

4. Conclusions

In conclusion, it is shown that the FMM long-range ordered magnetic state is metastable like a glass at low T in the LCMO sample, even when cooled in zero field. This state devitrifies on heating, akin to canonical glass, to equilibrium AFI phase. This glassy state ‘recrystallizes’ to AFI state on annealing and more easily by successive annealing, presumably through a heterogeneous nucleation process, producing a gigantic change in resistivity. The experiments are designed to probe different aspects of the glassy magnetic state, which can be created to varying extents in the very same sample by following different H - T paths below room temperature. Moreover, the glass formation can be tuned easily by H and T compared to tuning it by pressure and temperature for a conventional glass [30]. Our measurements show that *larger fractions of glass ‘recrystallize’ more easily*. Various intriguing features of this glassy system can be probed even in zero field by microscopic tools, mapping the spatially resolved change in phase fractions. This should shed more light on the physics of glasses.

Acknowledgment

DST, Government of India, is acknowledged for funding the 14T-PPMS-VSM at CSR, Indore.

References

- [1] Brawer S 1985 *Relaxation in Viscous Liquids and Glasses* (Columbus, OH: The American Ceramic Society)
- [2] Greer A L 1995 *Science* **267** 1947
- [3] Debenedetti P G and Stillinger F H 2001 *Nature* **410** 259
- [4] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
Mydosh J A 1993 *Spin Glasses: an Experimental Introduction* (London: Taylor and Francis)
- [5] Chattopadhyay M K, Roy S B and Chaddah P 2005 *Phys. Rev. B* **72** 180401(R)
- [6] Sengupta K and Sampathkumaran E V 2006 *Phys. Rev. B* **73** 020406(R)
- [7] Roy S B and Chattopadhyay M K 2007 *Eur. Phys. Lett. B* **79** 47007
- [8] Kushwaha P, Rawat R and Chaddah P 2008 *J. Phys.: Condens. Matter* **20** 022204
- [9] Sharma V K, Chattopadhyay M K and Roy S B 2007 *Phys. Rev. B* **76** 140401(R)
- [10] Roy S B, Chattopadhyay M K, Chaddah P, Moore J D, Perkins G K, Cohen L F, Gschneidner K A Jr and Pecharsky V K 2006 *Phys. Rev. B* **74** 012403
- [11] Roy S B, Chattopadhyay M K, Banerjee A, Chaddah P, Moore J D, Perkins G K, Cohen L F, Gschneidner K A Jr and Pecharsky V K 2007 *Phys. Rev. B* **75** 184410
- [12] Kumar K, Pramanik A K, Banerjee A, Chaddah P, Roy S B, Park S, Zhang C L and Cheong S-W 2006 *Phys. Rev. B* **73** 184435
- [13] Wu W, Israel C, Hur N, Soonyong P, Cheong S-W and De Lozane A 2006 *Nat. Mater.* **5** 881
- [14] Banerjee A, Mukherjee K, Kumar K and Chaddah P 2006 *Phys. Rev. B* **74** 224445
- [15] Banerjee A, Pramanik A K, Kranti K and Chaddah P 2006 *J. Phys.: Condens. Matter* **18** L605
- [16] Rawat R, Mukherjee K, Kumar K, Banerjee A and Chaddah P 2007 *J. Phys.: Condens. Matter* **19** 256211
- [17] Macià F, Hernández-Mínguez A, Abril G, Hernandez J M, García-Santiago A, Tejada J, Parisi F and Santos P V 2007 *Phys. Rev. B* **76** 174424
- [18] Chaikin P M and Lubensky T C 1995 *Principles of Condensed Matter Physics* (Cambridge: Cambridge University Press)
- [19] Chaddah P and Roy S B 1999 *Phys. Rev. B* **60** 11926
- [20] Imry Y and Wortis M 1979 *Phys. Rev. B* **19** 3580
- [21] Soibel A, Zeldov E, Rappaport M, Myasoedov Y, Tamegai T, Ooi S, Konczykowski M and Geshkenbein V 2000 *Nature* **406** 282
- [22] Roy S B, Perkins G K, Chattopadhyay M K, Nigam A K, Sohney K J S, Chaddah P, Caplin A D and Cohen L F 2004 *Phys. Rev. Lett.* **92** 147203
- [23] Manekar M A, Chaudhary S, Chattopadhyay M K, Singh K J, Roy S B and Chaddah P 2001 *Phys. Rev. B* **64** 104416
- [24] Chaddah P, Banerjee A and Roy S B 2006 *Preprint cond-mat/0601095*
- [25] Loudon J C, Mathur N D and Midgley P A 2002 *Nature* **420** 797
- [26] Levy P *et al* 2000 *Phys. Rev. B* **62** 6437
- [27] Debenedetti P G 1996 *Metastable Liquids* (Princeton, NJ: Princeton University Press)
- [28] Mahendiran R *et al* 2001 *Phys. Rev. B* **64** 064424
- [29] Banerjee A, Kumar K and Chaddah P 2007 *Preprint 0710.5585 [cond-mat]*
- [30] Mishima O and Stanley E 1998 *Nature* **396** 329