Interrupted Magnetic First Order Transitions and Kinetic Arrest probed with In-field Neutron Diffraction

V. Siruguri†, S.D. Kaushik†, S. Rayaprol†, P.D. Babu‡, P. Chaddah§, E.V. Sampathkumaran† A. Hoser‡, and C. Ritter#

†UGC-DAE Consortium for Scientific Research Mumbai Centre, R-5 Shed, BARC, Mumbai – 400085, India
§UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore – 452017, India
‡Tata Institute of Fundamental Research, Dr. Homi Bhabha Road, Colaba, Mumbai – 400005, India
¶Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
#Institut Laue-Langevin, 71 avenue des Martyrs, 38000 Grenoble, France

*Siruguri@csr.res.in

Abstract. In-field neutron diffraction studies were carried out on two compounds that exhibit magnetic first order phase transitions (FOPT). It is shown that the FOPT can be interrupted by an external magnetic field, resulting in a coexistence of kinetically arrested metastable states and equilibrium phases. Use of a novel protocol CHUF (Cooling and Heating under Unequal Fields) helps to determine the coexisting phase fractions and also to observe the devitrification of the kinetically arrested phase into the equilibrium phase, in a manner similar to that found in structural glassy systems.

1. Introduction:

Magnetic first order phase transitions (FOPT) are commonly found in a wide variety of materials like magnetic shape memory alloys, colossal magnetoresistance compounds, magnetocalorics and multiferroics. While in some cases the magnetic FOPT could be of the order-order type, driven by change of magnetic exchange interactions, it could also be accompanied by changes in volume or the symmetry of the crystal lattice. It is well-known that due to the presence of quenched disorder, there is a broadening of the FOPT which results in a distribution of transition temperatures [1-8]. Though temperature is the most commonly used thermodynamic variable for observing FOPT, pressure, magnetic and electric fields could also be useful second thermodynamic variables. It is possible to interrupt the FOPT by using an effective combination of these two variables, resulting in phase coexistence of magnetically ordered metastable states and equilibrium phases, collectively called kinetically arrested state or magnetic glass [1-6]. In such a state, the phase coexistence would persist down to the lowest temperature. The coexisting phase fractions could be quantified by employing the CHUF protocol (Cooling and Heating under Unequal Fields) [7, 8]. It is observed that the kinetically
arrested magnetic glass could devitrify into the equilibrium magnetic state at a lower temperature and subsequently re-enter the original high temperature magnetic phase. This is very similar to the case of conventional structurally disordered glasses that devitrify under the influence of temperature or strain. Since neutron diffraction can probe the magnetic and chemical structures of materials, it is capable of detecting the simultaneous presence of ferromagnetic (FM) and antiferromagnetic (AFM) phase fractions in the form of unique magnetic reflections for each phase. In combination with an external magnetic field and the CHUF protocol, this technique would be an ideal probe to differentiate between various coexisting phases as well as observe the devitrification of a kinetically arrested state [1, 2].

We describe here the kinetic arrest phenomenon observed through in-field neutron diffraction measurements in an archetypal half-doped manganite, La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) and a stoichiometric intermetallic compound Nd$_7$Rh$_3$. The systems were chosen as examples from a variety of compounds which show the first order magnetic phase transitions (FOPT). In these systems the field-induced magnetic transitions can be manipulated using external magnetic field as a second thermodynamic variable. In LCMO disorder is playing an important role in the phase transition and in Nd$_7$Rh$_3$ no chemical disorder is present.

ND experiments were carried out over a large region of field-temperature ($H$, $T$) space. Upon cooling, La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) undergoes a transition from a paramagnetic state to FM state at ~ 225 K and then, enters a charge-ordered antiferromagnetic (AFM) state at ~ 150 K through a first-order phase transition [1, 9]. In-field ND experiments, employing the CHUF protocol, show that the FOPT in LCMO could be completely interrupted, resulting in a metastable kinetically arrested state which, on subsequent heating in a lower field, devitrifies into its stable low temperature equilibrium AFM phase before reentering the higher temperature FM phase.

Phase coexistence seems quite ubiquitous to materials like LCMO which exhibit disorder-influenced FOPT but similar studies on stoichiometric compounds are quite rare, with notable exceptions like Gd$_5$Ge$_4$ and Nd$_7$Rh$_3$ [2, 10, 11]. Magnetic studies on Nd$_7$Rh$_3$ indicate the existence of a magnetic-field-induced FOPT [10, 11]. Nd$_7$Rh$_3$ also undergoes two transitions, the first one which is from a paramagnetic state to an AFM state at 32 K and later at 16 K, it undergoes a FOPT to another AFM state at 16 K, as borne out from magnetization measurements [10, 11]. The magnetic structure at low temperature was shown to be incommensurate and sine-wave modulated along the c-axis and the magnetic moments lie in the hexagonal basal plane [2]. ND measurements performed in presence of an external magnetic field show that the transition to the AFM state could be completely arrested when cooled under a field of 3 Tesla, and upon warming in a field of 0.2 Tesla, there is evidence of partial devitrification of the kinetically arrested state, giving rise to a seemingly complex magnetic order.

2. Experimental details

La$_{0.5}$Ca$_{0.5}$MnO$_3$ sample was synthesized by the conventional solid-state route and phase purity was confirmed by XRD. Detailed neutron diffraction (ND) measurements were carried out under various temperature and magnetic field conditions at a wavelength of 1.48 Å using the position-sensitive detector based focusing crystal diffractometer PD-3 installed by the UGC-DAE CSR Mumbai Centre at the Dhruva reactor, Trombay [12]. Room temperature neutron diffraction patterns for both the samples were analysed by Rietveld method for determining single-phase formation. DC magnetization was measured using a commercial 9 T PPMS-VSM (Quantum Design). Further details related to the sample are described elsewhere [1]. Neutron diffraction measurements on Nd$_7$Rh$_3$ were carried out as a function of temperature and magnetic field at the diffractometer D1B, Institut Laue Langevin, Grenoble and diffractometer E6, Helmholtz-Zentrum Berlin by making a special arrangement of collimators and direct-beam stop, so that the Q-range could be explored from upwards of 0.027Å$^{-1}$ at temperatures below and above the magnetic ordering [2].
3. Result and discussion

3.1. Half-doped charge ordered La$_{0.5}$Ca$_{0.5}$MnO$_3$

La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) is one of the widely studied compounds among manganites whose properties have been well documented by several research groups [13-17]. But very few have studied the interesting magnetic field dependent history effects [5, 7]. In an earlier paper [1], we measured magnetization curves in different warming fields after cooling from 300 K in a 6 Tesla field (CHUF protocol), reproduced here in figure 1. It is seen that cooling in a field of 6 Tesla results in a kinetic arrest of the FM phase down to the lowest temperature. Upon application of the CHUF protocol, a devitrification of the kinetically arrested, metastable, ferromagnetic phase to the equilibrium antiferromagnetic state and a subsequent re-entrance to the stable ferromagnetic state at a higher temperature is observed. It is also clear from figure 1 that for the 0.01 T FCW curve, the kinetically arrested ferromagnetic phase devitrifies by about 90% at 5 K. For higher warming fields, a lesser fraction of the metastable FM phase devitrifies at a higher temperature of 25 K into the stable low temperature antiferromagnetic phase. On further heating, the antiferromagnetic state re-enters the higher temperature ferromagnetic phase at ~230 K, and then finally goes into the paramagnetic phase. For warming fields above 3 T, the kinetically arrested phase no longer devitrifies at any intermediate temperature. ND measurements carried out in the (H, T) space reveal the microscopic nature of the coexisting phase fractions.

![Figure 1: Magnetization as a function of temperature employing the CHUF protocol (Reproduced from Ref. 1)](image)

Figure 2 shows the ND patterns of LCMO at 300 K and 9 K in zero field cooled condition and field-cooled in 7 Tesla at 9 K. Magnetic peaks corresponding to the CE-type AFM ordering are observed at 9 K at 20 ~ 14.03° and 15.87°, which are characterized by the two Mn sub-lattices, Mn$^{3+}$ and Mn$^{4+}$ with propagation vectors [0.5 0 0] and [0.5 0 0.5], respectively [15]. The ND pattern at the bottom of the figure corresponds to the condition where a magnetic field of 7 T was applied at 300 K and then the sample was cooled down to 9 K. In this pattern, it is clear that the magnetic peaks pertaining to the CE-type AFM order are completely absent and a strong enhancement in the intensities of the nuclear peaks occurs, indicating a well-defined ferromagnetic ordering. This is a clear indication that the FOPT to the AFM state has been kinetically arrested due to the field cooling of the sample. Refinement of the ND pattern at 9 K cooled in 7 Tesla using the Pnma space group along with a magnetic phase with ferromagnetic order gives a moment of 4.16 $\mu_B$ on Mn. This is consistent with the value obtained from magnetization measurements. Subsequently, CHUF protocol
was employed by reducing the field to 0.5 Tesla at 9 K and then, warming the sample in this field. ND patterns were collected at various temperatures during this warming cycle.

Figure 2: ND plots of LCMO at (a) 300K, (b) 9 K measured in zero field and (c) in 7T cooling filed.

The data are plotted in a sequence in figure 3. It is observed that up to 30 K, sample remains in a kinetically arrested, metastable ferromagnetic state as there is no signature of any change in the ND pattern to indicate any AFM ordering. On warming the sample beyond this temperature, the peaks corresponding to the CE-type AFM order (marked as asterisks) appear in the ND patterns and become well defined at 50 K, attaining roughly the same intensity as the ones observed in the zero field cooled case at 9 K. Appearance of these peaks signifies the de-arrest or devitrification of the arrested metastable FM phase and the setting in of the equilibrium AFM order. In the next cycle, the sample was cooled to 9 K in a field of 7 Tesla and then the warming field was set at 3 Tesla (CHUF protocol). The sample remains in a kinetically arrested metastable ferromagnetic state at 9 K when the external field is reduced to 3 Tesla. However, upon warming in a field of 3 Tesla, the devitrification of the kinetically arrested state now occurs only around 75 K, as evidenced by the appearance of weak magnetic peaks attributable to CE-type AFM order. It is further observed that the intensities of the CE magnetic peaks are much lower as compared to the previous case of warming in 0.5 Tesla field, implying a much higher fraction of the kinetically arrested phase remaining throughout this measurement cycle. Therefore, the dotted line shown in the inset of figure 2, connecting the two points at which the CE-type AFM peaks appear is taken to be the devitrification line or the \((H_k,T_k)\) line, separating the kinetically arrested phase from the equilibrium phase. The magnetic moment determined from refinement for the arrested FM phase at 100 K was calculated as 3.83 \(\mu_B\), while moments for the devitrified CE-AFM phase come out as 2.02 \(\mu_B\) for both Mn\(^{3+}\) and Mn\(^{4+}\). The AFM peaks disappear upon warming beyond 150 K, and the sample re-enters a fairly strong ferromagnetic phase at 175 K, consistent with the magnetization measurements. Refinement of the pattern at 175 K of this cycle gives a moment of 3.08 \(\mu_B\) for the re-entrant ferromagnetic phase.
In order to understand the microscopic situation in the sample, the Mn-O bond length and bond angles were calculated at various points in the ($H$, $T$) space and plotted in figure 4. It is well understood that the Mn–O bond lengths in LCMO at room temperature and in the CE-AFM phase are quite different due to Jahn–Teller distortion. It can be reasonably expected that the kinetically arrested FM phase would have almost undistorted MnO$_6$ octahedra, with all the Mn–O distances being approximately the same. Mn–O bond lengths and Mn–O–Mn bond angles at various temperature and field combinations, show some interesting observations. The values for 300 and 9 K show the expected changes in the bond lengths and angles at low temperature. However, for the kinetically arrested FM phase at 9 K, obtained by cooling in a field of 7 Tesla, and also when the field is reduced to 0.5 T (9 K, 0.5 T), the bond angles and lengths do not show any major differences from the 300 K values. A direct effect of the devitrification of the arrested phase at 35 K, 0.5 Tesla is seen in the Mn–O1 bond length and Mn–O1–Mn bond angle, which are comparable to the values of the (9 K, 0 T) set. A similar behaviour is seen at 100 K in the 3 T heating cycle. However, at 175 K warmed in 3 Tesla field, there is a re-entrant transition to the equilibrium FM phase, which again shows an undistorted situation, with the bond angles and lengths associated with O1 and O2 oxygens being similar.
3.2. Nd$_7$Rh$_3$
Nd$_7$Rh$_3$ exhibits two magnetic transitions, one at ($T_{N1}$ =) 32 K and another around ($T_{N2}$ =) 16 K. The uniqueness of magnetic ordering in this compound has been explained earlier [2]. When the sample is cooled below the magnetic ordering temperatures ($T_{N1}$ and $T_{N2}$), an intense AFM peak appears along with an enhancement in the intensities of some nuclear Bragg peaks indicating the coexistence of AFM and FM ordering in this system [2]. In figure 5, only the low-Q region, predominantly the AFM part, is focussed upon. The intense AFM peak at 1.6 K (well below the two AFM transitions and cooled in zero field) and centred at $Q = 0.07\text{Å}^{-1}$, can be observed (filled squares).

**Figure 4:** (a)Mn-O bond length and (b) Mn-O1-Mn bond angles for LCMO between 300 and 9 K under CHUF protocol

In the next step, the sample was cooled from 70 K to 1.6 K in a field of 3 Tesla and the ND pattern recorded at this stage is shown with red circles in figure 5. It can be clearly observed in this case that the strong AFM peak is completely suppressed, indicating that both the AFM transitions have been interrupted and the system goes into a kinetically arrested metastable state. Then, the field was
reduced to 0.2 Tesla after cooling in a field of 7 Tesla and the sample was warmed and ND patterns were recorded at different temperatures around $T_{N1}$ and $T_{N2}$. As the temperature reaches the vicinity of $T_{N2}$ (~ 16 K), there is a gradual increase in the intensity of the AFM peak suggesting that the sample has partly devitrified into its equilibrium low temperature AFM phase. On increasing the temperature further to 30 K, the magnetic peak becomes broadened and slightly stronger than it was at 15 K. An important observation from this figure is that the magnetic peak position in the devitrified state shifts from $Q \sim 0.07 \ \text{Å}^{-1}$ to $\sim 0.1 \ \text{Å}^{-1}$, clearly signifying that the underlying magnetic order is quite complex.

**Figure 6:** ND patterns of Nd$_7$Rh$_3$ measured as a function of temperature in using the CHUF protocol.

In figure 6, we plot the variation of the integrated intensity of the AFM peaks observed in the Q-range ~ 0.03 - 0.2 Å$^{-1}$. For the ND measurements carried out in zero field, the intensity of the magnetic peak (red squares) increases in the vicinity of $T_{N2}$, reaches maximum at around $T_{N1}$ and then reduces to about 1/3 rd of its peak value at $T = 1.6$ K. However, when the sample is cooled in 3 Tesla field (CF), and then warmed in zero field, the devitrification (indicated by increase in the intensity of the AFM peak) happens in the vicinity of 10 K, and at $T_{N1}$, it reaches its peak value. The process of devitrification shifts to higher temperatures when the sample is cooled in 3 Tesla (CF) and warmed in different fields (WF) as clearly seen in the figure. With the increasing strength of the field under which sample is warmed, the recovery of the magnetic peak intensity happens at higher temperatures, and as can be seen in the case of measurements done while warming in 0.2 Tesla and 0.4 Tesla fields, the full magnetic peak is observed above $T_{N2}$. The present experimental data clearly show that in-field neutron diffraction measurements using the CHUF protocol throw up some interesting possibilities of manipulating magnetic order. It would be worthwhile to carry out detailed experiments on single crystalline Nd$_7$Rh$_3$ to understand the field-induced changes to the magnetic structure and their implications on magnetism of this compound.

4. Conclusion

In-field neutron diffraction measurements performed on two systems that exhibit magnetic FOPT unambiguously demonstrate (i) the phenomenon of kinetic arrest, wherein the FOPT gets interrupted and the system enters a metastable arrested phase, (ii) that the kinetically arrested and equilibrium phases coexist and their phase fractions could be determined using the CHUF protocol, and (iii) de-arrest or devitrification of the arrested metastable phase in to the equilibrium phase in a manner similar to that found in structurally disordered glassy systems [19].
References

[1] Siruguri V, Babu P D, Kaushik S D, Biswas A, Sarkar S K, Madangopal Krishnan and Chaddah P, 2013 J. Phys.: Condens. Matter 25 496011 (and references therein)
[2] Rayaprol S, Siruguri V, Hoser A, Ritter C, and Sampathkumaran E V, 2014 Phys. Rev. B 90 134417 (and references therein)
[3] Banerjee A, Dash S, Lakhani A, Chaddah P, Chen X and Ramanujan R V, 2011 Solid State Commun. 151 971
[4] Schiffer P, Ramirez A P, Bao W, and Cheong S-W, 1995 Phys. Rev. Lett. 75 3336
[5] Banerjee A, Kumar K and Chaddah P, 2008 J. Phys.: Condens. Matter 20 255245
[6] Loudon J C, Mathur N D and Midgley P A, 2002 Nature 420 797; Dagotto E, Hotta T, and More A, 2001 Phys. Rep. 344 1
[7] Chaddah P, Kumar K and Banerjee A, 2008 Phys. Rev. B77 100402(R); Banerjee A, Kumar K, and Chaddah P, 2009 J. Phys.: Condens. Mater 21 026002
[8] Lakhani A, Banerjee A, Chaddah P, Chen X and Ramanujan R V, 2012 J. Phys.: Condens. Matter 24 386004 (and references therein)
[9] Radaelli P G, Cox D E, Marezio M and Cheong S-W, 1997 Phys. Rev. B 55 3015
[10] Sengupta K and Sampathkumaran E V, 2006 Phys. Rev. B 73 020406
[11] Sengupta K and Sampathkumaran E V, 2006 J. Phys.: Condens. Mater 18 L401
[12] Pimpale A V, Dasanmacharya B A, Siruguri V, Babu P D and Goyal P S, 2002 Nucl. Instrum. Methods A 481 615
[13] Babu P D, Das A and Paranjpe S K, 2001 Solid State Commun. 118 91
[14] Das A, Babu P D, Chatterjee S and Nigam A K, 2004 Phys.Rev. B 70 224404
[15] Wollan E O and Koehler W C, 1955 Phys. Rev. 100 545
[16] Goodenough J B, 1955 Phys. Rev. 100 564
[17] Rodriguez E E, ProffenTh, Llobet A, Rhyne J J and Mitchell J F, 2005 Phys. Rev. B 71 104430
[18] Tyson T A, Deleon M, Croft M, Harris V G, Kao C-C, Kirkland J and Cheong S-W, 2004 Phys. Rev. B 70 24410
[19] Wu W, Israel C, Hur N, Park S, Cheong S-W and de Lozanne A, 2006 Nature Materials 5, 881