Neutron diffraction evidence for kinetic arrest of first order magneto-structural phase transitions in some functional magnetic materials

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Abstract
Neutron diffraction measurements, performed in the presence of an external magnetic field, have been used to show structural evidence for the kinetic arrest of the first order phase transition from (i) the high temperature austenite phase to the low temperature martensite phase in the magnetic shape memory alloy \(\text{Ni}_{37}\text{Co}_{11}\text{Mn}_{42.5}\text{Sn}_{9.5}\), (ii) the higher temperature ferromagnetic phase to the lower temperature antiferromagnetic phase in the half-doped charge ordered compound \(\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) and (iii) the formation of glass-like arrested states in both compounds. The cooling and heating under unequal fields protocol has been used to establish phase coexistence of metastable and equilibrium states, and also to demonstrate the devitrification of the arrested metastable states in the neutron diffraction patterns. We also explore the field–temperature dependent kinetic arrest line \(T_K(H)\), through the transformation of the arrested phase to the equilibrium phase. This transformation has been observed isothermally in reducing \(H\), as also on warming in constant \(H\). \(T_K\) is seen to increase as \(H\) increases in both cases, consistent with the low-\(T\) equilibrium phase having lower magnetization.

(Some figures may appear in colour only in the online journal)

1. Introduction

A number of functional magnetic materials such as CMR manganites, magnetic shape memory alloys, intermetallics, multiferroics, etc, exhibit first order phase transitions (FOPTs) as a function of temperature, pressure or magnetic field. While the microscopic nature of these FOPTs has been extensively studied using temperature and pressure, the use of magnetic field as a useful thermodynamic variable in exploring these FOPTs at an atomic scale is not very common. However, in recent times, the study of first order transformation kinetics of these functional magnetic materials under the influence of a magnetic field has been the subject of intense experimental research [1–5]. In these materials, typically, the high temperature magnetic phase can be kinetically arrested when cooled under an appropriate external magnetic field, thereby inhibiting the transformation to the low temperature equilibrium phase. This kinetically arrested state has been shown to have coexisting phases of magnetically ordered metastable and equilibrium states.
and such a material has been termed [6, 7] as a ‘magnetic glass’. These studies attempt to investigate those regimes in knowledge space which have been hitherto unexplored, by using magnetic field as a useful thermodynamic variable. While the experimental techniques used in these studies are mostly based on transport and magnetization measurements, atomic scale measurements delineating the crystalline and magnetic structures as a function of magnetic field, for which neutron diffraction (ND) is a unique probe, have not been carried out so far. Certain classes of ferromagnetic shape memory alloys (FSMAs) like Co-doped NiMnSn, NiMnIn and NiMnAl undergo a kinetic arrest of the first order austenite to martensite transition [6, 8–10]. In these materials, the higher temperature austenite phase has a higher ferromagnetic moment as compared to the lower temperature martensite phase and this manifests itself as a sharp drop in magnetization in an $M$ versus $T$ measurement. By increasing the magnetic field of measurement, it has been observed that the kinetics associated with this first order transformation are hindered, and beyond a critical field they are completely arrested. Hence, there will be regions of field–temperature space where there will be a phase coexistence of metastable (arrested) or glass-like arrested states (GLAS) and equilibrium (transformed) states. If the lower temperature equilibrium (transformed) phase has a lower magnetization value than the high temperature austenite phase, it has been noted earlier that cooling in a certain higher field ($H_c$) and warming in a lower field ($H_w$) would lead to a de-arrest or devitrification of the GLAS [11]. On further warming, the devitrified state would undergo a reverse magnetic and structural transition to the high temperature, high moment austenite phase. This novel protocol of cooling and heating in unequal fields (CHUF) [11] offers an unambiguous method to observe if the GLAS devitrifies, thereby qualifying it to be called a magnetic glass. While the transitions in this material are predominantly structural, kinetic arrest has also been observed in materials which undergo a ferromagnetic to antiferromagnetic transition, for example the archetypal half-doped, charge ordered manganite La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) [12]. This compound is paramagnetic at room temperature, and upon cooling it first enters a ferromagnetic (FM) state at $\sim$225 K and then undergoes an FOPT into an antiferromagnetic (AFM) state at $\sim$150 K [13]. Transport and magnetization measurements employing similar measurement protocols show that the ferromagnetic phase can be kinetically arrested when cooled under an appropriate magnetic field through the FM–AFM transition, resulting in coexisting phases of metastable (arrested) FM states and equilibrium (transformed) AFM states [14]. The percentages of these phases would depend on the magnitude of the cooling field. CHUF protocol has been employed in the case of this compound also to demonstrate, through magnetization measurements, the devitrification of these glass-like arrested metastable states [12]. While transport and magnetization measurements do not provide information about the structures at the microscopic scale, ND is a powerful tool which can give information about not only the crystalline structure but also the magnetic structure. In particular, antiferromagnetic ordering of spins gives rise to unique reflections in ND whose origin is purely magnetic in nature. Therefore, it is expected that ND in the presence of an external magnetic field, when carried out using the above measurement protocol, would give unambiguous information about coexisting phases, crystalline and magnetic, in a material.

We present here ND studies, in the presence of an external magnetic field over a wide region of the field–temperature ($H$, $T$) space, of two widely different materials: (i) the ferromagnetic shape memory (FSMA) alloy Ni$_{37}$Co$_{11}$Mn$_{42.5}$Sn$_{0.5}$ and (ii) the half-doped manganite La$_{0.5}$Ca$_{0.5}$MnO$_3$. The former on cooling undergoes an FOPT from a high moment, austenite phase to a low moment, martensite phase, while the latter compound undergoes a predominantly first order magnetic transition from a ferromagnetic state to an antiferromagnetic state on cooling. We show evidence, for the first time, for the kinetic arrest of the first order structural and magnetic phase transitions in these compounds. In Ni$_{37}$Co$_{11}$Mn$_{42.5}$Sn$_{0.5}$, the first order austenite to martensite transition gets kinetically arrested when cooled under an appropriate magnetic field, and on heating from 2 K to room temperature in a different field, a subsequent devitrification of the arrested metastable austenite state to the martensite state takes place, followed by the re-entrant martensite to austenite transition. Similarly, in the half-doped La$_{0.5}$Ca$_{0.5}$MnO$_3$, we show that the higher temperature ferromagnetic phase gets kinetically arrested on cooling under a magnetic field and when subsequently heated under a different field, the metastable arrested ferromagnetic state devitrifies into the stable antiferromagnetic state before re-entering the higher temperature ferromagnetic state. The phase coexistence of the arrested metastable and equilibrium states employing the CHUF protocol is demonstrated. Finally, we explain the ($H$, $T$) phase diagram for the two compounds using the $T_K(H)$ line and attempt to draw analogies with the pressure–temperature ($P$, $T$) phase diagrams for metallic liquid germanium [15] and glassy water [16]. This study also brings out the versatility of magnetic field over hydrostatic pressure in that it is much easier to vary magnetic field as compared to pressure.

2. Experimental details

The Ni$_{37}$Co$_{11}$Mn$_{42.5}$Sn$_{0.5}$ buttons were made by vacuum arc melting high purity (99.99%) elements in appropriate proportions. The buttons were solutionized at 1273 K for 24 h in a sealed quartz ampule. High temperature differential scanning calorimetry (DSC) was used to confirm the two-phase melting behavior of this alloy and an extended homogenization treatment was given to ensure structural and chemical homogeneity. Characterization of this alloy has been carried out using optical and scanning electron microscopy, electron probe microanalysis, XRD and ND, transmission electron microscopy (TEM), DSC and DC magnetization. Electron probe microanalysis (EPMA) results confirmed that the alloy had the intended stoichiometry. Bulk cylindrical specimens of 5 mm diameter were prepared for
Figure 1. High temperature DSC plots of Ni$_{37}$Co$_{11}$Mn$_{42.5}$Sn$_{9.5}$ showing the two-phase incongruent melting behavior.

ND using electro-discharge machining, as powder samples do not undergo martensitic transformation in this alloy [5]. Nevertheless, one powder specimen was also prepared by crushing a part of the treated button and checked for room temperature structure. Specimens for TEM were prepared by slicing disks from an electro-discharge machined cylindrical rod of 3 mm diameter, followed by grinding and jet polishing with a Struers Tenupol-5 at 233 K, using a 10 vol% perchloric acid in methanol electrolyte. For ND measurements, the bulk cylindrical specimen was directly attached to the sample stick and inserted into the cryomagnet. The La$_{0.5}$Ca$_{0.5}$Sn$_{0.5}$Mn$_{0.5}$O$_{3}$ sample was prepared by the conventional solid-state route and the single-phase nature was confirmed using XRD, whose pattern matched well with literature reports. The polycrystalline powder sample was compacted into pellets and inserted into the vanadium sample holders. This avoided any preferential orientations of the grains under a magnetic field. The ND patterns were collected using the position-sensitive detector based focusing crystal diffractometer installed by the UGC-DAE CSR Mumbai Centre [17] at the Dhruva reactor, Trombay, at a wavelength of 1.48 Å in the temperature range of 2–300 K under different conditions of applied magnetic field up to 7 T. It was observed that the cylindrical FSMA sample consisted of extremely large grains, which manifest themselves in almost single-crystal-like behavior in the diffraction patterns. Hence, the sample was oriented such that two major reflections of the austenite phase at room temperature, namely (111) and (200), were clearly visible in the diffraction patterns. The sample was locked in this orientation for all subsequent measurements. DC magnetization was measured using a commercial 9 T PPMS-VSM (Quantum Design).

3. Results and discussion

3.1. Ferromagnetic shape memory alloy Ni$_{37}$Co$_{11}$Mn$_{42.5}$Sn$_{9.5}$

3.1.1. Alloy characterization. Figure 1 displays the high temperature DSC plots of this alloy. It clearly shows the two-phase incongruent melting behavior. Earlier, Watchel et al [18] noted the presence of a peritectic reaction in the ternary Ni$_{0.5}$Mn$_{0.5-x}$Sn$_{x}$ (0 ≤ x ≤ 0.5) pseudo-binary phase diagram. More recently, Yuhasz et al [19] also reported the problem of chemical and structural inhomogeneity that was prevalent in the ternary Ni–Mn–Sn alloys and was caused by this incongruent melting. It was thus very important to solutionize these alloys for an extended period of time to ensure single-phase and uniform microstructure. Microstructure in the as-solutionized condition shows the parent L2$_1$ phase (figure 2(a)), as confirmed by the (110) SAD pattern and its simulated key (figures 2(b) and (c)).

3.1.2. DC magnetization. Figure 3 shows the field cooled cooling (FCC) and field cooled warming (FCW) magnetization data at several different fields taken on a bulk sample of Ni$_{37}$Co$_{11}$Mn$_{42.5}$Sn$_{9.5}$. The observed thermal hysteresis in the FCC and FCW curves clearly indicates that there is an FOPT of high magnetization austenite phase to low magnetization martensite phase in the cooling cycle and the reverse transformation in the warming cycle. The magnitude of thermal hysteresis gradually increases as the field is raised and has maximum hysteresis for $H = 0.5$ T, and by a 2 T field the hysteresis disappears, as the austenite to martensite transformation is completely hindered by the field and the austenite phase is kinetically arrested at low temperatures. Such behavior was seen earlier [20] in similar types of compound. The austenite to martensite transformation start temperature ($M_S$ ∼ 181 K) in the cooling cycle and the reverse martensite to austenite transformation finish temperature ($A_F$ ∼ 230 K) in the heating cycle are nearly the same for fields up to 0.5 T. For 1.5 T, both these temperatures are shifted towards lower temperatures to about 145 K and 214 K, respectively. In other words, the temperature regime over which the hysteresis persists is nearly the same for fields up 0.5 T, and for 1.5 T it increases significantly although magnitude in terms of moment has come down. Both FCC and FCW curves merge and level off at low temperatures.
The magnetization value at 5 K increases systematically with field, as it will follow the $M-H$ curve of the martensite phase and also the phase fraction of austenite that remains arrested increases with field.

Figure 4 shows the $M$ versus $H$ isotherms taken at different temperatures. The final temperatures at which $M-H$ isotherms were recorded are reached by cooling the sample directly from 350 K in each case. For $T > 200$ K, the sample is in austenite phase and shows a ferromagnetic $M-H$ with high magnetization value (~130–145 emu g$^{-1}$). At 160 K, the sample is in martensite phase and one observes a ferromagnetic $M-H$ isotherm with low magnetization value (~55 emu g$^{-1}$). However, with increasing field, one observes a broad field-induced martensite to austenite transformation over a field range of 3–4 T. This trend continues as temperature is lowered to 5 K, and only the fields at which this transformation takes place go on increasing. At 5 K, even a field of 9 T is not enough to transform the system completely into the austenite phase.

In Figure 5, the field is raised to 9 T at 350 K and the sample is cooled to 5 K in field. Then, the field is isothermally reduced to zero at 5 K (red curve). This measurement shows that some devitrification of the arrested austenite phase takes place around 5 T (inset of figure 5), as indicated by the drop in the magnetization, which is still higher than the saturation magnetization (~60 emu g$^{-1}$) recorded at 5 K after cooling the sample in zero field (ZFC). Next, the CHUF protocol was employed to examine the kinetic arrest of the metastable austenite phase, its devitrification to the equilibrium martensite phase and their phase coexistence (figure 6). The sample was cooled in different fields ranging from 0.1 to 8 T down to 5 K and then the field is raised or lowered at 5 K to the value of the measuring field of 0.5 T and the measurements were carried out in the warming cycle. The ZFC magnetization curve, in which the sample was first zero field cooled down to 5 K and then the data were collected during the warming cycle in a field of 0.5 T, is also shown for comparison. For cooling fields which are less than 0.5 T, only one transition from a low magnetization phase to the high magnetization austenite phase is observed, which indicates that the low magnetization phase is the equilibrium martensite phase. On the other hand, for cooling fields that are greater than 0.5 T, a sharp drop in the magnetization at
low temperatures indicates that a devitrification is taking place from a glass-like arrested phase to an equilibrium martensite phase. On further increasing the temperature, a reverse transformation to the high temperature high magnetization austenite phase takes place. These observations are discussed along with the ND measurements made using the CHUF protocol in the next section.

3.1.3. Neutron diffraction. ND patterns of bulk cylindrical specimens show that the structure could be indexed to an $L_2_1$-structure with cell parameter of 5.957 Å (figure 7). The bulk sample exhibited strong large grain characteristics, behaving almost like a single crystal. The bulk sample was therefore oriented in such a way that the (111) and (200) reflections of the $L_2_1$ austenite phase were strongly visible in the ND pattern. The sample was cooled down to 2 K in this orientation, and the peaks associated with the martensite phase appeared. Though it is difficult to index the structure with the limited number of reflections, an attempt was made using a standard indexing program and it was observed that the martensite phase is 10M modulated with cell parameters $a = 4.338$ Å, $b = 5.534$ Å and $c = 21.21$ Å and $\beta = 92.55^\circ$. Four reflections belonging to the martensite phase have been clearly identified and marked in figure 7. A weak martensite peak is also observed at $\sim 31^\circ$, which could be indexed as the (020) reflection of the 10M martensite. On warming the sample to 300 K, there is a reverse transformation to the austenite phase in the neighborhood of 230 K. Next, a field of 7 T was employed at 300 K and the sample was cooled again to 2 K, and it was observed that the transition to the martensite phase was completely hindered, resulting in a kinetically arrested metastable austenite phase, as evident from the complete absence of any martensite reflections in the ND pattern at the bottom of figure 8. Employing the CHUF protocol, the sample was cooled in a field of 7 T from 300 K several times but warmed in different fields each time. The warming fields used were 0.5, 1.0, 1.5 and 2 T. When the field was reduced from 7 to 0.5 T for the first warming cycle, it was observed that the arrested austenite phase starts to devitrify at 2 K in a field of 0.5 T itself (figure 8), and the expected martensite peaks start appearing. In the next CHUF cycle, when the field was reduced from 7 to 1 T at 2 K, the sample remains in a kinetically arrested state at 2 K (figure 9), as evident from the absence of any peaks attributable to martensite phase. Devitrification sets in at around 10 K, as evidenced by the appearance of the 10M martensite lines mentioned above, and progresses with increasing temperature up to 230 K, beyond which the system re-enters the austenite phase. With warming fields of 1.0 T and above (figures 9–11), it is seen that the temperature at which the devitrification sets in increases with increase in the warming field. It is also observed that at this higher warming field the intensity of the 10M martensite lines decreases, implying that the phase fraction of devitrified phase is much lower. However, it is clear
from figure 3 that cooling and warming in fields greater than 2 T would cause the transition to be completely arrested, and no devitrification would be observed at any temperature below the standard martensite to austenite transition temperature. However, it must be kept in mind that, while magnetization data might indicate a complete arrest of the phase, the same data may not be able to detect the presence of a small amount of the converted martensite phase, and such a phase could be picked up by ND. This is evident from the very low intensity lines of the martensite phase in figure 11. It could be reasonably expected that there would be a complete arrest of the austenite phase at a higher field. It is important to note here that the quantity \((H_c - H_w)\), which is the difference between the cooling field \((H_c)\) and the warming field \((H_w)\), is always positive, and in the present case it becomes a precondition to observe (i) the de-arrest of the metastable austenite phase, which is similar to the phenomenon of devitrification of a conventional glass upon heating, and (ii) the transformation of the devitrified equilibrium state to the high temperature austenite phase, which is analogous to melting of devitrified glass. In figure 12, the temperature \(T_K\) at which devitrification, marked by the appearance of Bragg reflections attributable to the equilibrium martensite phase, sets in is plotted against the value of the warming field \(H_w\). It is observed that \(T_K\) increases with \(H_w\). The set of temperature points \(T_K\) collectively form the kinetic arrest line, which, when traversed across in the heating cycle, would result in the de-arrest of the metastable austenite phase to the equilibrium martensite phase. The line also indicates that at lower warming fields one would have a higher phase fraction of the martensite phase when compared to higher warming fields. In order to substantiate this, the integrated intensity of the \((103)M\) reflection at 140 K, which is the temperature at which the martensite phase fraction is expected to be at its peak value, is plotted as a function of \(H_w\), which is the field in which the ND patterns are recorded in each warming cycle (figure 13). Expectedly, the martensite phase fraction decreases at higher warming fields.

Figure 10. ND patterns obtained using the CHUF protocol. The sample was cooled from 300 to 2 K in a field of 7 T, which is isothermally reduced to 1.5 T. Data were taken in the warming cycle. Subscripts A, M and X have the same meaning as in figure 7.

Figure 11. ND patterns obtained using the CHUF protocol. The sample was cooled from 300 to 2 K in a field of 7 T, which is isothermally reduced to 2 T. Data were taken in the warming cycle. Subscripts A, M and X have the same meaning as in figure 7.

Figure 12. \(H-T\) diagram showing the kinetic arrest line, across which there would be a devitrification from the arrested metastable austenite phase to the equilibrium martensite phase.

Figure 13. Integrated intensity of the \((103)M\) reflection of the 10M martensite phase (obtained from figures 9–11) as a function of the warming field at 140 K.
3.2. Half-doped charge ordered compound La$_{0.5}$Ca$_{0.5}$MnO$_3$

3.2.1. DC magnetization. La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO) has been widely studied and its properties have been well documented by several authors. Therefore, we present here only those results which are new and form the basis for very interesting physics. The behavior of magnetization with temperature is similar to that observed in earlier studies [12, 14, 21–23]. The notable features are that (i) FCC and FCW curves at lower fields show thermal hysteresis accompanying the first order ferromagnetic to antiferromagnetic transition, (ii) the magnitude of this thermal hysteresis gradually decreases at higher fields, culminating in kinetic arrest of the FOPT, and the ferromagnetic order persists down to the lowest temperature, and (iii) on application of the CHUF protocol (figure 14), devitrification of the arrested, metastable, ferromagnetic phase to the equilibrium antiferromagnetic state and the subsequent re-entrance to the stable ferromagnetic state at a higher temperature is observed. Figure 15 shows the magnetization curves measured in different warming fields after cooling from 300 K in a 6 T field along with the 6 T FCC curve. For the 0.01 T FCW curve, the kinetically arrested ferromagnetic phase devitrifies by about 90% at 5 K. Subsequently, the remaining FM phase fraction further devitrifies at $\approx$25 K into the stable low temperature antiferromagnetic phase. On further heating, the antiferromagnetic state re-enters the higher temperature ferromagnetic phase at $\approx$230 K, and then finally goes into the paramagnetic phase. This behavior unfolds more explicitly at higher warming fields. It is also observed that the extent to which the kinetically arrested FM phase devitrifies becomes lesser with higher warming fields and that the temperature at which the devitrified phase re-enters the stable ferromagnetic phase decreases. This is clear from the higher moment values at 5 K for higher warming fields. For warming fields above 3 T, the kinetically arrested phase no longer devitrifies at any intermediate temperature.

![Figure 14. Magnetization as a function of temperature employing the CHUF protocol when the sample LCMO is cooled in a field of 6 T and measurements are carried out in different warming fields.](image)

![Figure 15. Rietveld fitted plots of LCMO at 300 and 9 K measured in zero field. Observed data are filled circles and the calculated pattern is shown as a continuous line through the data points. The difference pattern along with the Bragg ticks are shown below the patterns. For 9 K data, Bragg ticks indicate the phases (from top) majority nuclear phase, CE-AFM phase, and nuclear and FM phases of the high temperature residual phase.](image)

3.2.2. Neutron diffraction. Half-doped LCMO has been extensively studied using neutron diffraction [13, 24–28]. While some of the reports concentrate on determining the magnetic and crystalline aspects of the structure at different temperatures [13], some deal with the local structure and importance of the Mn–O bond lengths [26]. Magnetic-field-induced melting of the charge ordered state [27] and phase coexistence of antiferromagnetic and ferromagnetic states due to supercooling [28] have also been discussed. In the present ND measurements, we show that the FOPT from a high temperature ferromagnetic state to a low temperature antiferromagnetic state is completely or partially arrested (depending on the path taken during cooling in a magnetic field) due to hindered kinetics, resulting in GLAS. We also show that, by adopting the CHUF protocol, there is a phase coexistence of GLAS and equilibrium (transformed) states, and a de-arrest of the metastable states takes place as one crosses the ($H_K$, $T_K$) line. Figure 15 shows the Rietveld fitted patterns of LCMO at 300 and 9 K. The ND pattern at 300 K has been refined using the $Pmna$ space group. The oxygen occupancy for the 300 K pattern turns out to be $u = 2.987$, and for subsequent refinements $u$ was fixed at this value. Refinement of the ND pattern at 9 K was treated in the manner proposed by Radaelli et al [13], using the space group $Pmna$. The various parameters deduced from the Rietveld analysis are given in table 1. As expected, magnetic peaks corresponding to the CE type of ordering are observed at 9 K. This antiferromagnetic ordering is characterized by two Mn sublattices [24], Mn$^{3+}$ and Mn$^{4+}$. The propagation vectors are [1/2, 0, 1/2] for Mn$^{3+}$ and [1/2, 0, 0] for Mn$^{4+}$. It is also observed that a small amount of the room temperature phase persists at 9 K, and hence this was added as a minority phase.
to the refinement along with its corresponding ferromagnetic phase. The refinement shows that the percentage of this minority phase is about 6%. Refinement of the magnetic phase. The refinement shows that the percentage of this phase was reduced to 0.5 T (CHUF protocol), and the sample was heated to 300 K and again cooled down to 9 K in the presence of a magnetic field of 7 T. The ND pattern at 9 K cooled in 7 T field, shown in figure 16, is marked by a complete absence of any peaks, signifying the CE-type AFM order. This is a clear indication that the formation of the CE-AFM order has been kinetically arrested due to the c-axis for Mn⁴⁺ while they were constrained to be parallel to the c-axis for Mn⁵⁺. The refined moment values and the percentage phase fractions of the CE-AFM and FM phases are given in table 1. Next, the sample was heated to 300 K and again cooled down to 9 K in the presence of a magnetic field of 7 T. The ND pattern at 9 K cooled in 7 T field, shown in figure 16, is marked by a complete absence of any peaks, signifying the CE-type AFM order. This is a clear indication that the formation of the CE-type AFM order has been kinetically arrested due to the field cooling of the sample in a field of 7 T. The refinement of the ND pattern at 9 K cooled in 7 T using the Pnma space group along with a magnetic phase with ferromagnetic order gives a moment of 4.16 μB on Mn (table 1). This is consistent with the value obtained from magnetization measurements. After measuring at 9 K in a cooling field of 7 T, the field was reduced to 0.5 T (CHUF protocol), and the sample was warmed from 9 K in steps. The data are plotted in a sequence in figure 17. It is seen that, up to 30 K, the diffraction spectra remain unchanged and there is no signature of any change in the magnetic order, signifying that the sample remains in a kinetically arrested, metastable ferromagnetic state (magnetic GLAS) up to this temperature. At 35 K, there is an abrupt change in the spectrum, marked by the appearance of magnetic peaks corresponding to the CE-type AFM order (marked as asterisks). These peaks become well defined at 50 K and have roughly the same intensity as the ones observed in the zero field cooled case at 9 K. Therefore, 35 K represents the temperature around which the de-arrest or devitrification of the metastable glassy FM phase occurs and the equilibrium AFM order sets in. The percentage de-arrest would then be a function of the cooling and warming fields. In this case, the refinement of the pattern at 35 K taken during warming in a field of 0.5 T indicates that the de-arrest is almost complete, since the values of the moments on Mn⁴⁺ and Mn⁵⁺ are similar to the 9 K, ZFC case (table 1). On warming beyond 150 K, the sample re-enters a weak ferromagnetic state before finally entering the paramagnetic state at room temperature. In the next measurement cycle, the sample was cooled to 9 K in a field of 7 T, and then the warming field was set to 3 T (CHUF protocol). As in the earlier measurement cycle, the sample remains in a kinetically arrested metastable ferromagnetic state at 9 K when the external field is reduced to 3 T. However, upon warming in 3 T (figure 18), the devitrification of the kinetically arrested state takes place only around 75 K, as evidenced by the appearance of weak magnetic peaks attributable to CE-type AFM order. In contrast to the earlier field cycle, the intensities of the CE magnetic

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**Table 1. Structural parameters of La₀.₅Ca₀.₅MnO₃ obtained from Rietveld refinement of neutron diffraction data taken at different temperatures and magnetic fields.** Note that 0.5 and 3 T data are taken in the warming cycle after the sample is cooled in 7 T field from 300 K and reducing the field isothermally to the respective field values at 9 K.

| Parameter | 300 K, 0 T | 9 K, 0 T | 9 K, 7 T | 9 K, 0.5 T | 35 K, 0.5 T | 100 K, 3 T | 175 K, 3 T |
|-----------|------------|---------|---------|-----------|------------|------------|------------|
| a         | 5.4197(5)  | 5.4409(5) | 5.4155(5) | 5.4142(5) | 5.4398(5) | 5.4409(9)  | 5.4169(8)  |
| b         | 7.6462(7)  | 7.5280(7) | 7.6363(7) | 7.6354(7) | 7.5305(7) | 7.5303(11)| 7.6334(7)  |
| c         | 5.4268(6)  | 5.4741(6) | 5.4210(6) | 5.4202(6) | 5.4711(6) | 5.4767(8)  | 5.4247(8)  |
| V         | 224.89(6)  | 224.21(6) | 224.18(6) | 224.08(6) | 224.12(6) | 224.39(9)  | 224.31(7)  |
| La/Ca x   | 0.0147(4)  | 0.0228(4) | 0.0211(3) | 0.0215(5) | 0.0153(4) | 0.0162(3)  | 0.0239(4)  |
| z         | 0.4958(3)  | 0.4958(3) | 0.4964(1) | 0.4961(5) | 0.4988(1) | 0.4950(3)  | 0.4982(5)  |
| O1 x      | 0.4931(3)  | 0.4941(4) | 0.4893(3) | 0.4928(3) | 0.4907(4) | 0.5000(5)  | 0.4922(3)  |
| z         | 0.5617(1)  | 0.5660(4) | 0.5584(3) | 0.5583(4) | 0.5629(4) | 0.5705(4)  | 0.5574(3)  |
| O2 x      | 0.2759(3)  | 0.2696(4) | 0.2774(3) | 0.2751(4) | 0.2689(4) | 0.2764(4)  | 0.2758(4)  |
| y         | 0.0319(5)  | 0.0334(6) | 0.0338(5) | 0.0337(6) | 0.0332(6) | 0.0350(5)  | 0.0339(5)  |
| z         | 0.2224(3)  | 0.2275(4) | 0.2240(3) | 0.2205(4) | 0.2261(4) | 0.2221(4)  | 0.2233(4)  |
| B         | 0.64(7)    | 0.18(8)  | 0.03(8)  | 0.05(8)  | 0.05(8)  | 0.05(8)    | 0.05(8)    |
| Mn–O1     | 1.9410(4)  | 1.9167(6) | 1.9360(4) | 1.9353(5) | 1.9145(8) | 1.9218(9)  | 1.9340(4)  |
| Mn–O2     | 1.9371(4)  | 1.9403(6) | 1.9388(4) | 1.9270(5) | 1.9316(7) | 1.9490(8)  | 1.9404(4)  |
| Mn–O1–Mn  | 1.9505(4)  | 1.9649(6) | 1.9487(4) | 1.9605(6) | 1.9722(8) | 1.9700(9)  | 1.9483(5)  |
| Mn–O2–Mn  | 160.02(8)  | 158.17(9) | 160.85(8) | 161.05(8) | 159.07(10)| 156.81(10) | 161.31(8)  |
| Magnetic order | AFM     | FM        | FM        | AFM+FM    | AFM+FM    | AFM+FM     | AFM+FM     |
| AFM-Mn⁴⁺  | μ₁ (μB)    | 1.00(6)   | 1.00(6)   |           |           |            |            |
|           | μ₂ (μB)    | 2.31(5)   | 2.11(5)   | 2.20(10)  |            |            |            |
| Mn⁵⁺      | μ₂ (μB)    | 2.46(5)   | 2.26(5)   | 2.20(10)  |            |            |            |
| FM-Mn     | μ₂ (μB)    | 3.25(8)   | 4.17(4)   | 3.96(4)   | 3.73(4)   | 3.83(6)    | 3.08(7)    |
| R exp     | 10.7       | 19.0      | 16.1      | 19.7      | 16.5      | 25.7       | 23.4       |
| R exp     | 8.9        | 10.4      | 6.8       | 7.7       | 7.6       | 11.1       | 8.1        |
| χ²        | 16.9       | 23.3      | 18.8      | 28.3      | 17.9      | 40.1       | 40.3       |
| R exp     | 3.3        | 4.0       | 3.7       | 3.7       | 4.0       | 4.1        | 3.7        |
peaks are much lower, implying a much higher fraction of the kinetically arrested phase remaining throughout this measurement cycle. A refinement of the pattern at 100 K gives a moment of 3.83 \( \mu_B \) for the arrested FM phase, 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, in consonance with the magnetization measurements (figure 14). Refinement of the pattern at 175 K of this cycle gives a moment of 3.08 \( \mu_B \) for the re-entrant ferromagnetic phase (table 1).

It is observed that the arrest temperature \( T_K \), which has been monitored as the temperature at which the kinetically arrested metastable phase devitrifies, increases with the value of the warming field \( H_w \), as was the case with the FSMA sample, and this occurs only when the cooling field \( H_c \) is greater than the warming field \( H_w \). This is consistent with the earlier observation [6] that the condition \( H_c > H_w \) is required to observe the devitrification whenever the FOPT temperature and the supercooling limit \( T^\ast \) fall with increase in magnetic field. To draw an analogy, these observations are compared with the vitrification of liquid Ge under high pressure [15], wherein it was observed that monatomic liquid Ge forms a glass when quenched under a pressure of about 10 GPa. The metallic Ge glass so obtained transformed, under ambient decompression, from a high-density amorphous phase to a low-density phase. Similarly, Mishima and Stanley [16] discuss the one-phase collapse of ice \( H_6 \) from a high-density liquid to a high-density amorphous phase at high pressures. In the present cases, the transition temperature drops as the magnetic field rises, analogous to the melting point dropping with rising pressure in the case of germanium and water. However, unlike pressure, it is possible to tune a magnetic
field effortlessly, since it does not require a medium to propagate, and use it to study the microscopic nature of magnetic-field-induced transitions.

4. Conclusions

We have performed ND studies on two materials belonging to two different families of compounds, namely the magnetic shape memory alloy Ni$_{37}$Co$_{17}$Mn$_{25}$Sn$_{0.5}$ and the charge ordered manganite La$_{0.5}$Ca$_{0.5}$MnO$_3$. Using magnetic field as a useful thermodynamic variable and the CHUF protocol, we have shown structural evidence for the first time for (i) the kinetic arrest of the first order phase transition in both compounds, (ii) phase coexistence of the metastable arrested and the equilibrium phases, and (iii) devitrification of the metastable arrested phase.

Our diffraction studies have shown that the arrest temperature rises with increasing field, consistent with an earlier conjecture of Banerjee et al [29] and with an extension of the regime of validity of the Le Chatelier principle [30]. In cases where the low-$T$ equilibrium phase has a higher magnetization, transition temperature will rise with increasing field, and it was conjectured that the arrest temperature would fall with rising $H$. This has been confirmed through bulk and mesoscopic measurements in some manganites [1, 29, 30], in Gd$_5$Ge$_4$ [31], and in Ta-doped HfFe$_2$ [32]. Diffraction measurements under the CHUF protocol, with $H_w > H_c$, would confirm the earlier conjecture of the Le Chatelier principle being valid during the devitrification process; some of these materials that are suitable for ND studies shall be pursued.

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