

Unusual strain glassy phase in Fe doped $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$

R. Nevgi, and K. R. Priolkar

Citation: *Appl. Phys. Lett.* **112**, 022409 (2018);

View online: <https://doi.org/10.1063/1.5004054>

View Table of Contents: <http://aip.scitation.org/toc/apl/112/2>

Published by the [American Institute of Physics](#)

Articles you may be interested in

[Barocaloric and magnetocaloric effects in \$\(\text{MnNiSi}\)_{1-x}\(\text{FeCoGe}\)_x\$](#)

Applied Physics Letters **112**, 021907 (2018); 10.1063/1.5011743

[Influence of MgO barrier quality on spin-transfer torque in magnetic tunnel junctions](#)

Applied Physics Letters **112**, 022406 (2018); 10.1063/1.5005893

[Modulated spin orbit torque in a Pt/Co/Pt/YIG multilayer by nonequilibrium proximity effect](#)

Applied Physics Letters **112**, 022402 (2018); 10.1063/1.5006115

[Interface-induced perpendicular magnetic anisotropy of Co nanoparticles on single-layer h-BN/Pt\(111\)](#)

Applied Physics Letters **112**, 022407 (2018); 10.1063/1.5010836

[Influence of impurities on the high temperature conductivity of \$\text{SrTiO}_3\$](#)

Applied Physics Letters **112**, 022902 (2018); 10.1063/1.5000363

[Direction-division multiplexed holographic free-electron-driven light sources](#)

Applied Physics Letters **112**, 021109 (2018); 10.1063/1.5008985

Scilight

Sharp, quick summaries **illuminating**
the latest physics research

Sign up for **FREE!**

AIP
Publishing

Unusual strain glassy phase in Fe doped $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$

R. Nevgi and K. R. Priolkar

Department of Physics, Goa University, Taleigao Plateau, Goa 403206, India

(Received 11 September 2017; accepted 28 December 2017; published online 11 January 2018)

Fe doped $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$, particularly, $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$, despite having an incommensurate, modulated 7M martensitic structure at room temperature exhibits frequency dependent behavior of storage modulus and loss which obeys the Vogel-Fulcher law as well as shows ergodicity breaking between zero field cooled and field cooled strain measurements just above the transition temperature. Both frequency dependence and ergodicity breaking are characteristics of a strain glassy phase and occur due to the presence of strain domains which are large enough to present signatures of long range martensitic order in diffraction but are non-interacting with other strain domains due to the presence of Fe impurities. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5004054>

The term Glass describes a frozen state of a certain local order of a statistically disordered system in general. The glassy phase comprises a wide range of systems which include amorphous, ferroic systems, polymers, biological systems, etc.^{1,2} A strain glass is a ferroelastic state with a short range ordering of the elastic strain vector. It is analogous to spin glass and relaxor in ferromagnetic and ferroelectric states, respectively.³ The evidence for the existence of the strain glass phase in the off stoichiometric NiTi martensitic binary alloy ($\text{Ni}_{50+x}\text{Ti}_{50-x}$, $x \geq 0.15$) is first reported in Ref. 4. It is believed to be a result of sufficient doping of point defects (Ni at the Ti site) suppressing the long range ordering of the elastic strain vector (martensitic transformation) preferring a B2 \rightarrow R (trigonal) over B2 \rightarrow B19 (monoclinic) transformation. The strain glass is unable to reach the long range strain order and is locked in a state in which short range persists.^{4,5}

Apart from Ni rich NiTi alloys, the strain glassy phase has been found in other impurity doped alloys including $\text{Ti}_{50}\text{Ni}_{50-x}\text{D}_x$ (D = Fe, Co, Cr, and Mn)^{6,7} with D acting as an impurity. A similar situation is seen in $\text{Ti}_{50}\text{Pd}_{50-x}\text{Cr}_x$ (Ref. 8) wherein a crossover from martensitic transition to strain glass transition is observed at a critical doping concentration. The magnetic shape memory alloy $\text{Ni}_{55-x}\text{Co}_x\text{Fe}_{18}\text{Ga}_{27}$ also exhibits characteristics of strain glass transition at a critical Co level of 10%.⁹

In the literature, a strain glassy phase has been clearly distinguished from pre-martensitic tweed formation.³ Strain glass exhibits a frequency dependent anomaly in its dynamical mechanical properties around the transition temperature T_g . The anomaly is the existence of a dip in the ac storage modulus curve and the corresponding peak in the loss ($\tan \delta$) curve. A frequency dependence of T_g obeying the Vogel-Fulcher law is also seen.¹⁰ The other trait of glass transition which distinguishes it from pre-martensitic tweed is the existence of ergodicity breaking evidenced in zero field cooled (ZFC) and field cooled (FC) experiments. Strain glass transition is also characterized by an invariant crystal structure across the glass transition. The strain glassy phase is identified with the formation of nanosized domains with the frozen elastic strain vector and long range structural order, and consequently, the crystal structure does not change.

Fe doping in martensitic Ni-Mn-In alloys results in the suppression of T_M and strengthening of ferromagnetic interactions.^{11,12} The suppression is rather rapid and is explained to be due to the destruction of Mn-Ni-Mn antiferromagnetic interactions and formation of Fe-Fe ferromagnetic interactions due to site occupancy disorder.¹² The question then arises is to whether Fe doping in martensitic Ni_2MnIn alloys also results in impeding long range ordering of the elastic strain vector and formation of the strain glass phase similar to the one observed in impurity doped NiTi alloys. We attempt to answer this question by studying the structural, thermal, and frequency dependent elastic properties of $\text{Ni}_2\text{Mn}_{1.5-x}\text{Fe}_x\text{In}_{0.5}$ alloys. Here, the undoped $\text{Ni}_2\text{Mn}_{1.5}\text{In}_{0.5}$ is martensitic below 422 K, and our results show that Fe doping results not only in a decrease in T_M but also in the formation of an unusual strain glassy phase.

The synthesis of $\text{Ni}_2\text{Mn}_{1.5-x}\text{Fe}_x\text{In}_{0.5}$ ($x = 0, 0.025, 0.05, 0.075, 0.1, 0.15, \text{ and } 0.2$) was carried out by arc melting in the argon atmosphere by taking stoichiometric proportions of each constituent element. The beads of each alloy formed were melted several times by flipping over to ensure homogeneity. A part of each bead was cut into suitable sizes and the remaining powdered. The powder covered in tantalum foil and the pieces were encapsulated in evacuated quartz tube, annealed at 750 °C for 48 h and subsequently quenched in ice cold water. Room temperature x-ray diffraction (XRD) patterns of the powdered alloys were recorded using Mo K_α radiation in the angular range of 10° to 70° to obtain structural information. The prepared compositions were checked by scanning electron microscopy with energy dispersive X-ray (SEM-EDX) measurements. All alloys were found to have compositions within 2 to 5% of stoichiometric values. To confirm martensitic transformation temperatures, differential scanning calorimetry (DSC) and four probe resistivity measurements were performed. DSC measurements were accomplished using Shimadzu DSC-60 on 6 to 7 mg pieces of each alloy crimped in aluminium pans, and resistivity measurements were concluded using Oxford Instruments Optistat DNV on rectangular pieces of about 9.7 mm in length. Frequency dependent measurements of AC storage modulus and internal friction ($\tan \delta$) were carried out using a dynamic mechanical analyzer (Q800, TA Instruments). Measurements

were carried out as a function of temperature, using the 3 point bending mode by applying a small AC stress that generated a maximum displacement of $5\ \mu\text{m}$ at different frequencies in the range of 0.1 Hz to 7 Hz on samples cut in rectangular bars of $(10\ \text{mm} \times 3\ \text{mm} \times 1\ \text{mm})$ dimensions.

The room temperature x-ray diffraction patterns presented in Fig. 1 show a modulated martensitic structure for samples with $x \leq 0.1$, indicating that these alloys undergo martensitic transformation at a temperature $T_M >$ room temperature. On the other hand, compositions $x=0.15$ and $x=0.2$ show a two phase pattern consisting of the cubic austenite and modulated martensite phases (indicated in Fig. 1 with * and + signs, respectively). Estimated phase fractions of cubic and martensitic phases from Le Bail refinement were obtained as 57.8:47.2 for $x=0.15$ and 89.5:10.5 for $x=0.2$ alloys, respectively. This indicates that Fe doping results in the growth of the cubic phase at the expense of the martensitic phase. The rate of growth of the cubic phase suggests a possibility of the existence of a minor cubic phase even in the $x=0.1$ alloy but present diffraction measurements did not detect the presence of any impurity phase. The austenite to martensite transition temperature was determined through the DSC measurements which are depicted in Fig. 2. The transformation to martensitic state reflects as exothermic and endothermic peaks during warming and cooling cycles, respectively. The hysteresis in positions of the peaks during warming and cooling confirms the first order nature of the transformation.

The sensitivity of T_M to the Fe content is evident through the fact that the transition temperature decreases sharply with a small doping concentration of Fe at the expense of Mn in $\text{Ni}_2\text{Mn}_{1.5-x}\text{Fe}_x\text{In}_{0.5}$. While the undoped alloy transforms from the austenitic to martensitic state at 422 K, in $\text{Ni}_2\text{Mn}_{1.425}\text{Fe}_{0.075}\text{In}_{0.5}$, the transformation occurs at 355 K. Interestingly, the composition $x=0.1$ seems to show a broad feature over an otherwise sharp transition observed in the DSC when a material transforms via a first order transition (Fig. 2). Such a nearly vanishing DSC peak has been

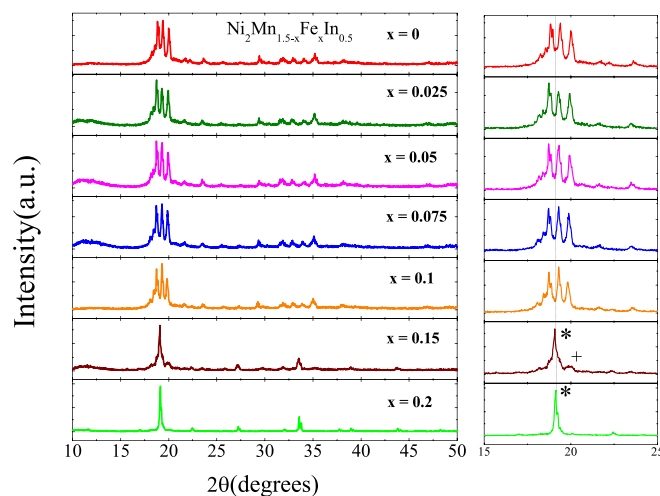


FIG. 1. X-ray diffraction patterns of $\text{Ni}_2\text{Mn}_{1.5-x}\text{Fe}_x\text{In}_{0.5}$ indicating the incommensurate 7M modulated martensitic structure in the alloys $x=0, 0.025, 0.05, 0.075,$ and 0.1 . The phase co-existence can be clearly seen in the composition $x=0.15$ in the form of cubic and martensitic peaks marked as * and +, respectively, while $x=0.2$ shows an almost fully grown cubic phase.

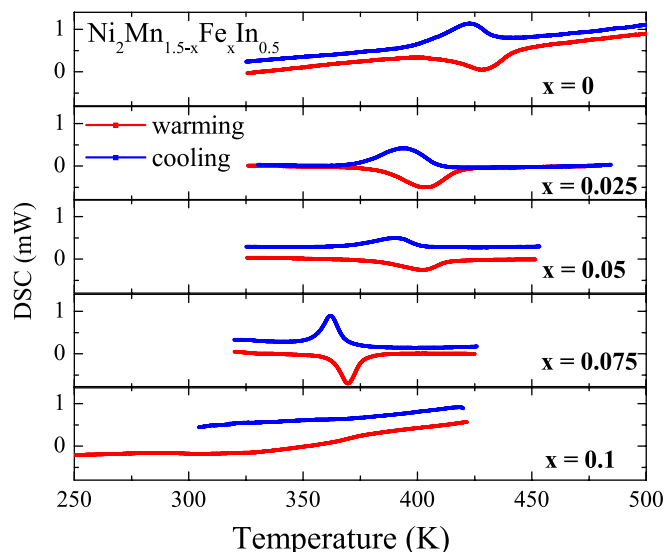


FIG. 2. Differential scanning calorimetry plots during warming and cooling cycles in $\text{Ni}_2\text{Mn}_{1.5-x}\text{Fe}_x\text{In}_{0.5}$ ($x=0, 0.025, 0.05, 0.075,$ and 0.1).

attributed to short range ordering of the strain vector across the ferroelastic transition.³ It may be noted that the compositions with $x=0.15$ and $x=0.2$ do not show any transition down to the lowest measured temperature despite having a sizable ($>10\%$) fraction of the martensitic phase. Recently, crystallization of strain glass via an isothermal transformation has been reported in Ni rich NiTi alloys.¹³ In order to check such a possibility of isothermal growth of the martensitic phase in these alloys, DSC measurements were performed on the $x=0.1$ alloy using the same procedure as described in Ref. 13. No growth of a heat loss peak indicating the appearance of the martensitic phase was observed in these measurements. Therefore, the observed weak feature in DSC of the $x=0.1$ alloy could possibly be due to a continuous transformation due to compositional disorder or due to the existence of more than one structural phases wherein one of them is martensitic and its transformation is inhibited by the other impurity phases. Compositional disorder can be ruled out in $x=0.1$ as the SEM-EDX measurements report its composition to be $\text{Ni}_{2.00}\text{Mn}_{1.36}\text{Fe}_{0.14}\text{In}_{0.50}$ which is quite close to the prepared composition.

Resistivity measurements (Fig. 3) carried out on the compositions $x=0.05$ and $x=0.075$ expectedly show a sharp rise in resistance values as a signature of first order transition in the same temperature range as DSC measurements. In the case of the $x=0.1$ alloy, a much slower rise in resistivity is observed around 350 K, which is consistent with the broad transition in the DSC thermogram. Additionally, a weak first order transition is seen at $\sim 380\ \text{K}$ in the resistivity measurements of the $x=0.1$ alloy [see inset of Fig. 3(g) for clarity]. While the weak first order transition at 380 K could be due to martensitic transformation which explains the observation of the modulated structure in XRD at room temperature, the broad transition at 350 K could be due to short range order of the elastic strain vector. The presence of two transitions, one hinting at long range martensitic order and the other pointing to some sort of glassy phase transition, indicates the presence of phase co-existence in this alloy, and hence, further on in this letter, we focus our attention on alloy compositions $x \leq 0.1$.

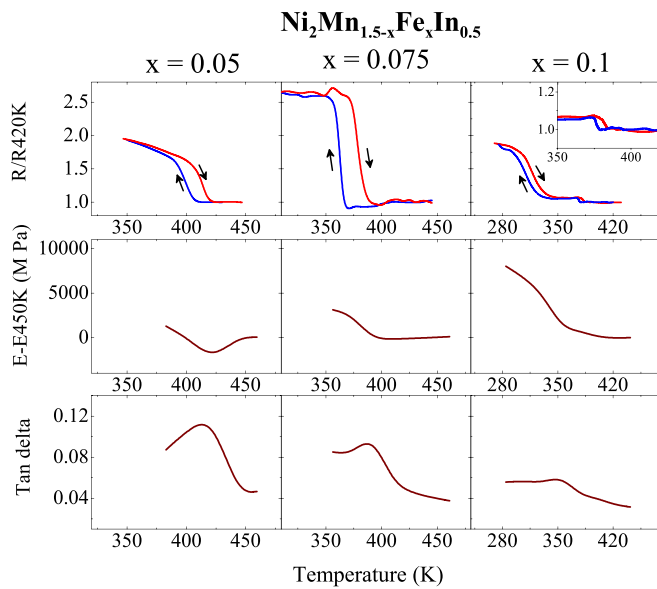


FIG. 3. The temperature dependence of the normalized resistance and the ac storage modulus and $\tan \delta$ in $\text{Ni}_2\text{Mn}_{1.5-x}\text{Fe}_x\text{In}_{0.5}$.

Impurity doping in martensites is known to be an initiator of a conjugate transition from the austenitic phase to a strain glass phase which is a frozen disordered state of short range ordered strain vectors. The characteristics of such a glassy state are (a) frequency dependence of ac modulus/loss exhibiting behavior according to the Vogel-Fulcher relation, (b) ergodic symmetry breaking between ZFC and FC curves around the glass transition temperature, (c) invariance of the average structure, and (d) existence of short range order in the glassy state. Here, $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$ though exhibiting a long range ordered martensitic structure at room temperature shows a vanishingly small DSC peak and a broad transition in resistivity at about 350 K which are considered to be signatures of glassy dynamics. To understand this seemingly paradoxical situation better, AC storage modulus and internal friction or loss were measured as a function of temperature at several different frequencies between 10 Hz and 0.1 Hz and compared with other alloys with a lower Fe content. Behavior of storage modulus and loss ($\tan \delta$) for three alloy compositions, $x = 0.05$, 0.075 , and 0.1 , at a characteristic frequency of 5 Hz is presented in Fig. 3.

Temperature evolution of ac storage modulus and $\tan \delta$ exhibit a dip followed by a sharp increase and a peak at around T_M in all alloy compositions up to $x = 0.075$ (Fig. 3), respectively. The intensity of the peak as well as the sharpness of the rise however decreases with the increasing Fe content. In $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$, the sharp anomaly converts to a broad feature followed by a slow rise of storage modulus at about 350 K which is in good agreement with the results obtained from DSC and resistivity measurements. The peak in $\tan \delta$ observed at the same temperature and classified as T_g exhibits a frequency dependence as can be clearly seen in Fig. 4. Such a frequency dependence is absent in all other alloys with a lower Fe content. A plot of T_g versus $\log(\text{frequency})$ presented in the inset of Fig. 4 can be fitted to the Vogel Fulcher law, $\omega = \omega_0 \exp[-E_a/k_B(T - T_0)]$, where E_a is the activation energy and T_0 is the “ideal glass” temperature. This indicates a possibility of a glassy transition in

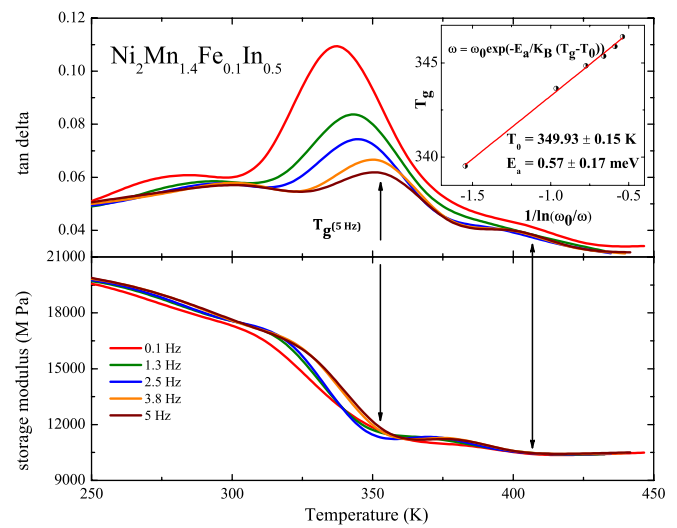


FIG. 4. The frequency dependent behavior of ac storage modulus and $\tan \delta$ observed in $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$. The inset shows the logarithmic dependence of the peak in $\tan \delta$ along with a best fit to Vogel Fulcher relation (solid line).

$\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$. The relative shift of glass transition temperature is assessed by a parameter $k = \frac{\Delta T_g}{T_g(\Delta \log \omega)}$ and is estimated to be 0.025. In comparison, the value of the k parameter in Ni rich NiTi alloys is about 0.02.⁴ This slightly higher value of the k parameter in $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$ could be due to the presence of larger sized domains in the present alloy as compared to those in Ni rich NiTi alloys. Another interesting aspect to be noted is the presence of a smaller but distinct feature in temperature dependence of $\tan \delta$. This feature appears between 375 K and 400 K (marked by arrow in Fig. 4) and matches with the weak first order transition seen in the resistivity measurements on this alloy.

To further check the presence of the strain glassy phase in $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$, history dependence of strain during zero field cooled (ZFC) and field cooled (FC) cycles was carried out and the results are presented in Fig. 5. A clear deviation between the two curves, which is considered as a critical proof of existence of the strain glassy phase, can be seen

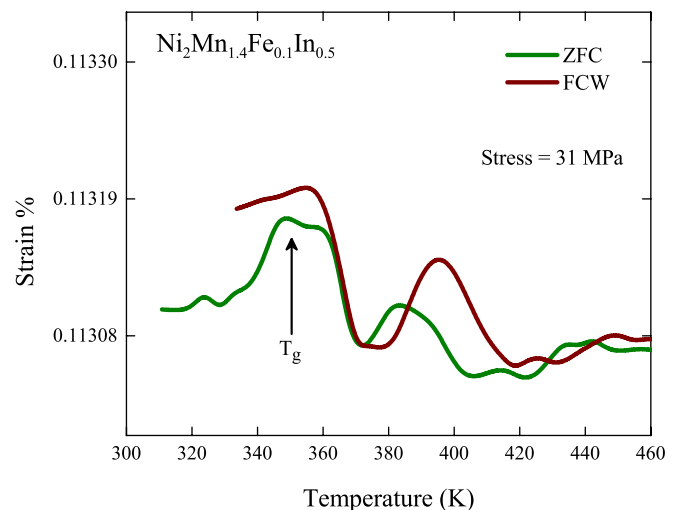


FIG. 5. % Strain as a function of temperature recorded during zero field cooled and field cooled cycles at 6 Hz.

from ~ 363 K which is above $T_g = 350$ K. This confirms that $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$ is indeed a strain glass.

The question then arises about the room temperature structure of $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$ and the presence of a first order transition in its resistivity measurement. For a strain glass, the structure is expected to be invariant across the transition. However, the $x=0.1$ alloy exhibits a martensitic structure. In magnetic cluster glasses, there are examples of materials exhibiting glassy characteristics and yet presenting long range magnetic order. Recently, such a phenomenon has been explained to be due to the presence of clusters large enough to show characteristics of long range magnetic order in neutron diffraction but still exhibit glassy behavior due to limited interaction between clusters.¹⁴ The presence of such large strain domains separated by nonmartensitic regions in $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$ cannot be ruled out. Structural studies on higher Fe content ($x \geq 0.15$) alloys show the presence of two, austenitic and martensitic, structural phases. Such a scenario, wherein either the concentration of the cubic austenitic phase is quite low or the grains are not large enough to be detected in XRD, could be also present in the $x=0.1$ composition. It is in fact supported by the presence of a weak but distinct features corresponding to a first order transition in resistivity and ac storage modulus and loss measurements. It appears that $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$ consists of clusters that are largely deficient in Fe and hence undergo martensitic transition at a temperature very close to that of the undoped alloy. These clusters are large enough to show signatures of the incommensurate modulated 7M structure in XRD but have very limited interactions with other similar clusters due to the presence of minor Fe rich impurity phases. The slightly higher value of the k parameter (0.025) as compared to that observed in NiTi alloys also supports the presence of large clusters. Such an unusual strain glassy phase reported here needs to be investigated further using temperature dependent structural and local structural techniques.

In conclusion, Fe doping in $\text{Ni}_2\text{Mn}_{1.5-x}\text{Fe}_x\text{In}_{0.5}$ results in the reduction of martensitic transition temperature with increasing x as evidenced from exothermic and endothermic peaks during warming and cooling cycles in DSC. Although at room temperature $\text{Ni}_2\text{Mn}_{1.4}\text{Fe}_{0.1}\text{In}_{0.5}$ exhibits an incommensurate, modulated 7M martensitic structure, its DSC thermograms

show a nearly vanishing feature indicating the presence of short range ordering of the strain vector. A frequency dependent behavior of storage modulus and loss which obeys the Vogel-Fulcher law and the presence of ergodicity breaking between zero field cooled and field cooled strain measurements just above the transition temperature confirm the presence of a frozen glassy state below $T_g = 350$ K. Despite the martensitic structure, the presence of a strain glassy phase can be explained to be due to the presence of strain domains which are large enough to present signatures of long range martensitic order in diffraction but remain non-interacting with each other due to the presence of impurity phases rich in Fe.

The authors wish to acknowledge the financial assistance from the Science and Engineering Research Board, Government of India under the Project No. SB/S2/CMP-0096/2013.

¹C. A. Angell, *Science* **267**, 1924 (1995).

²A. P. Sokolov, *Science* **273**, 1675 (1996).

³X. Ren, "Strain Glass and Strain Glass Transition," in *Disorder and Strain-Induced Complexity in Functional Materials*, Springer Series in Materials Science, edited by T. Kakeshita, T. Fukuda, A. Saxena, and A. Planes (Springer, Berlin, Heidelberg, 2012), Vol. 148.

⁴S. Sarkar, X. Ren, and K. Otsuka, *Phys. Rev. Lett.* **95**, 205702 (2005).

⁵J. Zhang, Y. Wang, X. Ding, Z. Zhang, Y. Zhou, X. Ren, D. Wang, Y. Ji, M. Song, K. Otsuka, and J. Sun, *Phys. Rev. B* **84**, 214201 (2011).

⁶D. Wang, Z. Zhang, J. Zhang, Y. Zhou, Y. Wang, X. Ding, Y. Wang, and X. Ren, *Acta Mater.* **58**, 6206 (2010).

⁷Y. Zhou, D. Xue, X. Ding, Y. Wang, J. Zhang, Z. Zhang, D. Wang, K. Otsuka, J. Sun, and X. Ren, *Acta Mater.* **58**, 5433 (2010).

⁸Y. Zhou, D. Xue, X. Ding, K. Otsuka, J. Sun, and X. Ren, *Appl. Phys. Lett.* **95**, 151906 (2009).

⁹D. P. Wang, X. Chen, Z. H. Nie, N. Li, Z. L. Wang, Y. Ren, and Y. D. Wang, *Europhys. Lett.* **98**, 46004 (2012).

¹⁰X. Ren, Y. Wang, Y. Zhou, Z. Zhang, D. Wang, G. Fan, K. Otsuka, T. Suzuki, Y. Ji, J. Zhang, Y. Tian, S. Hou, and X. Ding, *Philos. Mag.* **90**, 141 (2010).

¹¹M. K. Chattopadhyay, K. Morrison, A. Dupas, V. K. Sharma, L. S. S. Chandra, L. F. Cohen, and S. B. Roy, *J. Appl. Phys.* **111**, 053908 (2012).

¹²D. N. Lobo, K. R. Priolkar, S. Emura, and A. K. Nigam, *J. Appl. Phys.* **116**, 183903 (2014).

¹³Y. Ji, D. Wang, X. Ding, K. Otsuka, and X. Ren, *Phys. Rev. Lett.* **114**, 055701 (2015).

¹⁴E. T. Dias, K. R. Priolkar, A. K. Nigam, R. Singh, A. Das, and G. Aquilanti, *Phys. Rev. B* **95**, 144418 (2017).