Multiple Ferroic Glasses Via Ordering

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Abstract: Structural glasses are characterized by the loss of long-range translational and rotational symmetry. In the last two decades, however, it has been discovered that materials that exhibit ferroic (ferromagnetic, ferroelectric and ferroelastic) phase transformations may also exhibit glassy behavior, in which the ferroic degrees of freedom (magnetization, polarization, strain) exhibit a loss of long-range translational symmetry. A consequence of this loss of long-range symmetry is the suppression of the ferroic phase transitions. Moreover, these unique glassy systems exhibit dynamic and thermodynamic behavior analogous to regular structural glasses. Conventionally, the onset of glassy behavior is brought about by the introduction of spatial heterogeneities, typically originating from point defects, particularly in the case of strain glasses. Here, we demonstrate, for the first time, that configurational order/disorder in a single ferromagnetic alloy ($\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.6}\text{In}_{13.4}$) can be used to stabilize both strain and magnetic glasses. The control of the degree of configurational order—through simple heat treatment schedules—, and simultaneous application of stress and magnetic field enabled us to observe a Kauzmann point, that is, the collapse of the entropy difference between a crystalline and a glassy phase. Systematic investigation of the transformation behavior in this system as a function of heat treatment enabled us to observe four kinds of solid-solid phase transitions (ferromagnetic-paramagnetic, martensitic transformation, strain and magnetic glass) in a single composition. The alloy investigated can be used to further elucidate the nature of ferroic glass transitions and their coupling.

Keywords: Ferroic glasses; strain glass; martensitic transformation; shape memory alloys; magnetic glass.

1. Introduction

1.1 Overview

To understand the similarities between conventional (structural), magnetic and strain glasses, it is instructive to first examine glass-forming silica as an example [1]. Figure 1A schematically shows a pure molten silicate undergoing an isothermal phase transformation from an amorphous liquid to a symmetric crystal at its melting point (T_m). However, the amorphous structure can be stabilized at slow cooling rates by introducing Na defects that frustrate the crystal's long range crystalline translational/rotational symmetry. This allows the liquid's amorphous liquid structure to be super-cooled past T_m producing a second order transition (T^*) and frozen below the second-order glass transition temperature (T_g). The unfrozen glass's glassy relaxation dynamics follow a Vogel-Fulcher-Tamman type behavior between T^* and T_g , while the frozen glass's glassy relaxation dynamics follow an Arrhenius type behavior below T_g . The critical transitions and the resulting relaxation dynamics associated with them are used to identify and characterize the behavior in conventional glassy phases. Similar relaxation dynamics and transitions have been used to describe ferroic glasses [2-7] even though the transition is between two crystalline solids instead of an amorphous liquid and crystalline solid.

The schematic of entropy vs temperature response of a strain glass is shown in Figure 1B in the alloys under study, as an example, which shows thermo-elastic martensitic transformation. As the high temperature austenite phase is cooled, a first-order phase transformation to martensite occurs at the martensite start temperature (T_{Ms}). This transformation is characterized by diffusionless atomic displacements, resulting in a spontaneous breaking of the symmetry of the high temperature phase. According to conventional theories about the strain glass transition, once a critical concentration of point defects is present, the martensitic transformation is replaced by a supercooling transition at T^* followed by a second order strain glass freezing at T_g . Current understanding of strain glass behavior suggests that defects cause local random lattice distortions along the austenite-to-martensite deformation path. The resulting random planar spacing along preferred crystallographic directions produces an anisotropic glassy structure that frustrates the long-range martensitic transformation strain [8]. In other words, the atoms in the anisotropic glass have translational symmetry along all directions (like a traditional crystal) except along the austenite to martensite deformation pathway where a non-periodic amorphous structure exists (like a traditional glass). Interestingly, the resulting strain glass can exhibit superelasticity

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4 between T^* and T_g and shape memory effect below T_g [4]. To date, evidence for strain glass
5 transition has been found in off-stoichiometric NiTi(Fe,Co,Cr,Mn), NiCoMnGa, and NiCoFeGa,
6 NiMnIn(Fe, Cr), CeFe, (La, Pr, Ca)MnO₃ alloys. However, there is still no conclusive evidence
7 as to the nature of the point defects responsible for the onset of strain glass behavior [2,4-11].
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12 The same analogy with conventional structural glasses can be extended to magnetic glasses
13 as displayed in Figure 1C [12]. An ordinary paramagnetic to ferromagnetic transition is
14 characterized by magnetic spin alignment along a single direction that creates long-range
15 translational/rotational magnetic symmetry. In contrast to the martensitic transformation, the
16 ferromagnetic transition is second-order and strengthens during cooling below the Curie
17 temperature (T_C). If sufficient disorder exists in a ferromagnetic system (due to point defects or
18 due to competing ferro and anti-ferro magnetic interactions), spins are prevented from arranging
19 themselves in patterns with long-range symmetry. The ‘amorphous’ magnetic structure is
20 supercooled below T^* and then freezes below a critical temperature (T_f). These spin glasses were
21 first discovered by doping Cu with Mn magnetic point defects, although in this case the magnetic
22 spins are isolated and only interact weakly with each other [13]. In contrast, in some other
23 magnetic glasses the magnetic spins are arranged into clusters that have local ferromagnetic
24 ordering, but do not form long-range symmetric structures with each other [14,15]; a structural
25 glass analogy is a semi-crystalline material. Evidence of spin and cluster spin glasses have been
26 observed in GdGe, the low temperature martensite phase of CuZnAlMn shape memory alloys
27 (SMAs) and NiCoMnSn magnetic SMAs (MSMAs) [14-18].
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42 Another type of glass, not shown in Figure 1, similar to the strain and magnetic glasses
43 described above can be observed when electric dipole alignment inside a material does not have
44 long-range translational or rotational symmetry. These ferroelectric glasses are commonly
45 referred to as relaxor ferroelectrics and share similar Vogel-Fulcher-Tamman and Arrhenius
46 relaxation in their unfrozen and frozen disordered states, respectively, with the glasses described
47 above [19,20]. Relaxor ferroelectric glasses have been observed simultaneously with strain
48 glasses in materials such as PbLa(ZrTi)O (PLZT) perovskites where a martensitic transformation
49 is coupled to a polarization [20].
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57 A common phenomenon described as “tweed” or cross-hatched microstructures have been
58 observed in materials that undergo thermo-elastic martensitic transformations. These structures
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are different from the martensitic transformation and are thought to be a pre-cursor to the martensitic transformation, typically appearing above T_{Ms} , as the austenite begins to explore configurations compatible with the martensitic structure [21]. Unlike strain glasses, they are characterized by propagation of modulations throughout the microstructure of the material. Studies on NiTi and NiAl/NiTiFe [22] have indicated that the tweed structures and strain glasses share a similar underlying physical basis, but they manifest from different causes. Large elastic anisotropy in the austenite phase stabilizes tweed structures while disorder from defects is thought to stabilize the strain glass state [21,22]. Additionally, tweed structures are unable to completely suppress the martensitic transformation like strain glass transitions do.

1.2 The Kauzmann Paradox

Although the frustrated microscopic degrees of freedom are different from one another, the different kinds of glasses described above can be treated in a similar thermodynamic manner at macroscopic scales. One similarity is the extrapolated entropy of the high temperature phase intersecting the entropy curve of the low temperature phase in Figure 1A-1C. At this critical temperature, known as the Kauzmann point (T_K), the entropies of the high and low temperature phases become identical [23, 24]. This critical point is considered a paradox in the case of structural glasses because it ~~is~~ ~~was~~ deemed impossible for a frozen amorphous phase, with high configurational entropy contributions from disorder, to have lower entropy than a highly ordered crystalline phase [24].

Due to a glass' tendency to undergo a glass transition before the Kauzmann point is reached, T_K has only been directly observed in special cases such as polymer chains with very small breadth-distribution and Helium III and IV [24]. Figure 2 displays a schematic diagram for Helium III or IV adapted from [24] where direct observation of a Kauzmann point occurs in the pressure-temperature phase diagram. The slope of the first order phase transformation line can be used to determine the relative entropy of the two phases by using the Clausius-Clapeyron relationship $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$. The volume of the liquid phase is assumed to remain greater than the crystalline phase, which makes the ΔV term negative. At high temperatures, the $\frac{dP}{dT}$ slope is positive which indicates that ΔS must be negative and the entropy of the crystalline phase is less

than the liquid phase. Similarly, below T_K , $\frac{dP}{dT}$ becomes negative which indicates that ΔS is positive and the liquid phase has lower entropy than the crystalline phase. The point at which the slope changes from positive to negative is defined as T_K and has been calculated to be $\sim \frac{1}{2} T_m$ for many pure metallic elements [19,25]. To prevent violation of the third law of thermodynamics, another Kauzmann point must exist as the system approaches absolute zero, i.e. the $\frac{dP}{dT}$ slope approaches zero as $T \rightarrow 0$ [24]. The Clausius-Clapeyron relationship for He III and He IV represents a hysteresis-free first order transition and care must be used when extending this analysis to the first order transition with hysteresis found in SMAs and MMSMAs.

1.3 Alloy Selection

To date, the strategy to stabilize a strain glass in materials that show first order martensitic transformation has been to add impurities that suppress the martensitic transformation and promote the formation of a glassy state beyond a critical concentration [2,6-9]. In the present work, the same strain glass stabilization is shown to occur by manipulating the degree of configurational order and defect clusters in a single alloy composition. Control of configurational order also leads to the onset of cluster spin glass stabilization in the material's martensitic phase of the material. By holding the composition constant in the alloy under investigation, i.e. $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.6}\text{In}_{13.4}$ magnetic shape memory alloy (MSMA), the strain glass / cluster spin glass is examined in this work without affecting the alloy's electron-to-atom ratio (e/a ratio) or magnetic valence that have considerable influence on its properties [26-28]. Different degrees of configurational order, which produce different defect concentrations and distributions, were achieved in this off-stoichiometric Heusler alloy through heat treatments between 673 K and 1073 K. It is will be shown here in the present work that these heat treatments affect the material's configurational order and point defect concentration of the material which enhances T_C and T_f , suppresses T_{Ms} and ultimately stabilizes the formation of a strain glass phase.

NiCoMnIn was selected because it has been studied extensively in the MSMA literature, can be easily grown into single crystals, and is expected to exhibit responses representative of the materials that show strain or spin glasses by compositional control [29-37]. Single crystals were used to eliminate grain boundary effects. The B2 ordered crystals were subjected to secondary

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4 heat treatments between 673 K and 1073 K for three hours and then water quenched (WQ) to
5 increase the $L2_1$ ordering. The impact of B2 vs $L2_1$ ordering on the martensitic and
6 ferromagnetic transitions, as well as on the onset of the ferroic glass transitions were
7 investigated. The present work differs from the previous ones that utilizes changes in chemical
8 composition to observe traditional and ferroic glasses [2, 4-11,13-18].
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16 **2. Experimental Procedures**

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19 Elemental Ni, Co, Mn and In were induction melted and pre-cast into a copper chilled mold
20 with a nominal $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.6}\text{In}_{13.4}$ composition. The single crystals were then grown from these
21 ingots in a He environment using the Bridgman technique. Single crystal samples were wire
22 electro-discharge machined to $2 \times 2 \times 4 \text{ mm}^3$ for uniaxial compression testing and $0.5 \times 2 \times 26 \text{ mm}^3$
23 for dynamic mechanical analysis (DMA) in single cantilever beam mode. The long axes for
24 uniaxial compression and for DMA testing were cut along the [100] crystallographic orientation.
25 The crystals were sealed in quartz ampoules and homogenized at 1173 K for 24 hours, then water
26 quenched (WQ). They were then sealed under argon again in quartz ampoules and subjected to
27 secondary heat treatments between 673 K and 1073 K for 3 hours then WQ prior to magneto-
28 thermo-mechanical testing. Samples for Transmission Electron Microscopy (TEM) were cut
29 from single crystals with the (110) direction perpendicular to the sample surface and twin jet
30 electro polished.
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41 DC magnetic properties were measured using a Quantum Design Superconducting Quantum
42 Interference Device – Vibrating Squid Module (SQUID-VSM) and AC magnetic properties were
43 measured using a traditional extraction style SQUID magnetometer with an AC magnetic coil.
44 For the DC experiments, all samples were cooled to 5 K under zero magnetic field, a 0.05 T
45 biased field was applied and the sample heated and cooled between 5 K and 400 K. The first
46 heating is referred to as the zero field cooled (ZFC) response while the cooling under 0.05 T and
47 the subsequent heating under the same field is referred to as the field cooled (FC) response. For
48 AC magnetic measurements, the real part of the magnetization was measured every 1°C in a
49 30°C temperature window, spanning the cluster spin glass freezing temperature, using 0.05T
50 amplitude AC magnetic excitation frequencies logarithmically spaced between 1Hz and 1000Hz.
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The magnetization and strain vs. magnetic field responses under constant uniaxial compression were characterized using a custom built micro-magneto-thermo-mechanical test frame (micro MTM) [35]. The micro-MTM's body and inner components of the micro MTM are made of from precipitation hardened nonmagnetic Cu-Be and can apply compressive stresses on the specimens using 316L stainless steel Belleville springs driven by a screw mechanism. The Belleville springs were specially designed such that the change in applied stress due to thermal expansion during heating/cooling experiments in the temperature range of 300K to 4.2K is not more than ± 3 MPa for the given sample dimensions. Displacements with an accuracy of ± 0.0001 mm are measured using a miniature capacitive sensor that is capable of measuring the displacement at temperatures as low as 4.2 K and magnetic fields as high as 18 Tesla. The micro MTM was placed in an extraction type 18 T magnet to obtain magnetization and strain measurements on the specimens under magnetic fields from 0 to 18 Tesla, test temperatures ranging from 4.2 to 300 K and stress levels up to 125 MPa.

Using the micro-MTM, the samples were loaded to -80 MPa at room temperature, cooled below the martensitic transformation temperature then heated to the desired temperature for magnetization testing. Calibration of the load cell verified that the -80MPa stress was held constant between ± 5 MPa during temperature sweeps and phase transformation. The magnetic field was ramped to 18T at a rate of 0.3 T per minute.

DMA testing was conducted in single cantilever beam mode using a Mettler Toledo TT-DMA. The sample was cooled to 125 K under 0 MPa then heated at 5 K per minute to 400 K while measuring the logarithmically spaced frequency dependent elastic modulus (E') between 0.2 Hz and 25 Hz. The compliance modulus between logarithmically spaced 0.05 Hz and 6.3 Hz was measured at 150 K, 175 K, 200 K and 225 K to determine the characteristic relaxation time (τ_0) at each temperature.

3. Experimental Results

3.1 Magnetic and Martensitic Transitions

Magnetization vs. temperature plots for samples that underwent martensitic transformation were used to determine the spin glass freezing (T_f), martensite start (T_{Ms}) and Curie (T_C) temperatures. as shown in Figure 3A displays an example of these transformations for the 873 K

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4 – 3hr – WQ sample. After cooling under 0T, known as zero-field cooled (ZFC) case, and
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6 applying a 0.05 T field, a peak at 33 K is observed in the initial heating response as the 873 K –
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8 3hr – WQ sample undergoes a second order magnetic glass transition at T_f . Further heating
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10 causes little change in magnetization until the first order transformation from weakly magnetic
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12 martensite to ferromagnetic austenite occurs between the austenite start (T_{As}) and austenite finish
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14 (T_{Af}) temperatures. The magnetization is then stabilized until a large transient occurs at the
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16 austenite T_C . Upon cooling, the ferromagnetic transition occurs in the austenite with no thermal
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18 hysteresis. The austenite to martensite transformation is hysteretic with T_{Ms} and the martensite
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20 finish (T_{Mf}) temperature usually below T_{As} and T_{Af} .

21 The martensite's magnetization of the martensite is path-dependent below T_f . The bifurcation
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23 of the magnetization in the ZFC and field cooled (FC) paths—a signature for non-ergodicity—
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25 is a well-documented indicator of glassy behavior [12]. In the case of magnetic glasses, this
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27 results from the magnetic spins (isolated or cluster-like) being frozen in a completely random
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29 configuration in the ZFC condition and a field-biased configuration for the FC condition. Similar
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31 responses have been observed in the strain and electric polarization responses in strain glasses
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33 and ferroelectric relaxors, respectively, with the ZFC peak corresponding to the glass transition
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35 or freezing temperature [3,38].

36 Further investigation of the AC magnetic response around T_f reveals the existence of glassy
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38 relaxation. The frequency dependent peak shift observed in Figure 3B has a Vogel-Fulcher-
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40 Tamman relationship with $T_f = 33.3\text{K}$ as shown by the inset. Although further testing using
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42 higher order magnetic susceptibility measurements is required to elucidate the true magnetic
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44 nature of these complex magnetic systems, we refer to this transition as a cluster spin glass
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46 transition due to the glassy relaxation dynamics.

3.2 Strain Glass Transitions

52 In the case of the 673 K – 3hr – WQ samples, the thermally induced martensitic
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54 transformation was completely suppressed. No sign of martensitic transformation was detected
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56 either with differential scanning calorimetry down to 120K or SQUID down to 6K. The 673 K –
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58 3hr – WQ sample condition was also subjected to the dynamic mechanical analysis (DMA)
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60 displayed in Figure 4 to characterize its relaxation dynamics. Above 300K the storage modulus
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(E') is frequency-independent and the material stiffens with decreasing temperature. This stiffening is expected from traditional crystalline materials. Interestingly, the traditional crystalline response is interrupted by a second order transition (T^*) at 261 K followed by decreasing stiffness with decreasing temperature. A larger frequency dependence is also observed during and after the second order transition which indicates a transition from a stable crystal to an unfrozen glass. In contrast, thermally transforming SMAs show a first order change in DMA analysis localized around the first order martensitic transformation. The inset in Figure 4 displays the characteristic relaxation time τ_0 determined using the same frequency dependent compliance scheme introduced in [39]. The τ_0 trend has a Vogel-Fulcher-Tamman relationship with temperature; indicative of an unfrozen strain glass with 104.4 K being the glass transition temperature (T_g). This calculation from relaxation experiments has been shown to coincide with the strain glass transition from direct experiments in NiTi [39]. Since the available experimental testing systems were not capable of conducting DMA below 150K or ZFC – FC experiments down to 100K, direct experimental measurement of T_g for the strain glass behavior was not possible; T_g could only be determined using the extrapolation from the Vogel-Fulcher-Tamman relationship.

3.3 Kauzmann Point

To determine T_K for the 673 K – 3hr – WQ condition, the martensitic transformation was first stabilized with stress (-80 MPa) and the critical magnetic fields for martensitic transformation were then determined at various temperatures. In other words, even though the material do not exhibit thermally-induced martensitic transformation, it is possible to induce the transformation with external stress. The -80 MPa ~~load~~ stress was sufficient to stabilize the martensite upon cooling, in a similar manner to stress induced crystallization in amorphous polymers. Once the martensite is stabilized below T^* (Figure 4), the critical magnetic field levels to trigger martensite to austenite reverse transformation were determined at various temperatures. The magnetization (solid) and strain (dashed) vs magnetic field response for the [100] oriented compression sample under -80 MPa is displayed in Figure 5. Following the 150 K test, the sample begins in the martensitic state at 0 T. The martensite is quickly magnetized to a low saturation point and the strain remains fairly constant as the magnetic field is ramped between 0

1 T and 3 T. As the magnetic field is increased beyond 3 T the first-order martensitic transformation from martensite to austenite occurs as shown by the large increase in magnetization and decrease in transformation strain. The transformation is completed around 5 T as shown by the magnetization and strain saturation between 5 T and 10 T. As the magnetic field is removed, the strain and magnetization remain fairly constant and retraces the magnetic loading path until the austenite to martensite transformation occurs between 2.5 T and 0.5 T. The critical fields required for martensitic transformation were determined using the slope intercept method shown in the 110 K curves. As the testing temperature decreases from 190K to 30K, the critical magnetic field required for the martensite to austenite transformation increases while the critical field for austenite to martensite transformation first increases then decreases. These experiments also show that the magnetic saturation of the martensite phase remains lower than the magnetic saturation of the austenite phase down to 30 K.

Figure 6 displays the temperature dependent critical magnetic fields for the martensite start (H_{Ms}) and austenite finish (H_{Af}) magnetic fields determined from the magnetization and strain measurements given in Figure 5. The equilibrium magnetic field (H_0), defined as the average of the forward and reverse transformation critical fields, is plotted as well. This equilibrium magnetic field is considered to be the equilibrium point in the critical field – temperature phase diagram. Calculating H_0 using this averaging technique has been shown to be rate-independent in NiCoMnIn when comparing slowly ramped and rapidly pulsed magnetic field induced phase transformations [36].

Using the analysis scheme described for Figure 2, a Kauzmann point at 80 K is observed. Here, the temperature dependent slope of the equilibrium magnetic field for phase transformation is used to determine the relative entropy of the two phases by applying the Clausius-Clapeyron relationship $\frac{dH_0}{dT} = \frac{-\Delta S^{A \rightarrow M}}{\Delta M^{A \rightarrow M}}$; where $\Delta M^{A \rightarrow M} = M^M - M^A$ and $\Delta S^{A \rightarrow M} = S^M - S^A$ are the differences in magnetization and entropy, respectively, between martensite and austenite. It should be noted that although the strain is changing while ramping the magnetic field, the stress remains constant and therefore does not appear in this Clausius-Clapeyron relationship. The martensite magnetization remains lower than austenite magnetization, evident in the magnetization curves in Figure 5, which makes the $\Delta M^{A \rightarrow M}$ term negative throughout the experimental temperature range. Above 80 K, the $\frac{dH_0}{dT}$ slope is negative indicating that the

$\Delta S^{A \rightarrow M}$ term is negative and thus the austenite phase's entropy is greater than the martensite phase's entropy. As the temperature decreases, the slope increases until it becomes positive below a critical point at $T_K^{-80\text{MPa}} = 80 \text{ K}$ and the entropy of the austenite phase's entropy becomes lower than the entropy of the martensite phase's entropy. In other words, the relative thermodynamic stability of the two phases is different above and below 80 K. The expectation that stress suppresses the Kauzmann point [24] indicates that $T_K^{0\text{MPa}}$ is higher than 80K and may be above the calculated T_g of 104.4K (Figure 4).

4. Discussion of the Results

4.1 The Role of Ordering Heat Treatments

Secondary heat treatments on NiMn based MMSMAs between 673 K and 1073 K change the atomic order [40] and in the present study we show that these heat treatments in turn change all the other material transitions. The B2 or CsCl structure displayed in Figure 7A is created when one atom type, Ni and Co in this case, occupy the body centered lattice location and the other lattice sites are another atom type, either Mn or In. This is the ordered structure obtained from quenching the homogenized sample from sufficiently high temperatures. If the sample is held below the B2-to-L2₁ transition temperature, further ordering to the structure, displayed in Figure 7B, occurs as the Mn and In atoms settle into separate lattice locations. To obtain a complete L2₁ ordered system (Figure 7), a stoichiometric composition of (Ni/Co)₂MnIn is required in the NiCoMnIn alloy. While the selected Ni₄₅Co₅Mn_{36.6}In_{13.4} composition is off this stoichiometry, L2₁ ordering still occurs below ~896 K and its morphology can be varied by varying the time and temperature of secondary heat treatments [30]. Figure 8 displays dark field TEM images of the austenitic L2₁ characteristic (111) superlattice diffraction spot for the samples heat treated between 673 K and 1073 K for 3 hours. The bright areas correspond to L2₁ ordering while the dark areas are B2 ordered. The L2₁ morphology is ~10 nm or less in size for Figure 8d - 973 K, Figure 8e - 1073 K and Figure 8f - 1173 K heat treated samples. The 873 K heat treated sample displayed in Figure 8c contains larger sized L2₁ regions that are less uniform while the 773 K heat treated sample displayed in Figure 8b exhibits 100-150 nm rectangular L2₁ regions. The fully arrested 673 K sample displayed in Figure 8a exhibits a uniform distribution of L2₁ regions that are 15 nm or less. These B2-L2₁ ordering boundaries can be varied without changing the

composition and are thought to be the source of the strain and cluster spin glasses. More systematic studies must be conducted to determine the exact defect structures that create the strain glass phenomenon.

4.2 Phase Diagram

The extracted T_C , T_{Ms} , T_f , T_g , T^* and T_K critical transitions for all the samples heat treated between 673 K and 1073 K have been assembled into the phase diagram displayed in Figure 9. The heat treatments between 773 K and 1073 K lead to a transformation sequence similar to the response displayed in Figure 4. In this region of Figure 9, T_C and T_f increase linearly while T_{Ms} decreases linearly with decreasing heat treatment. The samples heat treated between 673 K and 773 K also respond similarly to the sample in Figure 5, but T_f increases exponentially while T_C continues to increase linearly. T_{Ms} first decreases exponentially then rises rapidly indicating unstable supercooling in the gold triangular phase field. The 673 K heat treatment has a very different response that originates from the absence of a martensitic transformation under 0 MPa. Instead of T_{Ms} , a super cooling transition at T^* that falls along the linear extrapolation of T_{Ms} . This gives evidence to T^* originating from a transition between stable austenite and an unfrozen strain glass at the extrapolated T_{Ms} point. The unfrozen strain glass is then expected to freeze below T_g . The T_{Ms}^{-80MPa} value obtained during cooling under -80 MPa, obtained from the experiments in Figure 6, displays a continued exponential trend in T_{Ms} allowing completion of the unstable supercooled phase field (gold triangle). While T_K^{-80MPa} falls below T_g , as expected from the relationship between T_K and T_g in Figure 1B, the 0MPa Kauzmann point may be above T_g .

4.3 Magnetic Transitions

Due to the oscillatory nature—ferromagnetic-to-antiferromagnetic—of the Mn-Mn magnetic exchange constants (Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange [41-43]), re-arranging Mn atoms as the alloy goes from B2 to $L2_1$ ordering, the degree of configurational order is expected to influence the magnetic properties of Mn-containing Heusler alloys. The increases in T_C between the 1073 K and 673 K heat treatments suggest greater volume fraction of $L2_1$

ordered domains, which is experimentally demonstrated by diffraction experiments on $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.7}\text{In}_{13.3}$ [26]. While the L2_1 ordering occurs in the high temperature austenite phase, the martensite's T_f of the martensite is still affected because it inherits the austenite's morphology and defect structures shown in Figure 8. The cluster spin glass in Figure 1C displays a possible ferromagnetic, blue, and antiferromagnetic, yellow, domain structure created by Mn anti-site defects that change the average Mn-Mn distance. It is believed that these magnetic defects stabilize the cluster spin glass causing the increases in T_f .

4.4 Martensitic and Strain Glass Transitions

Decreasing heat treatment temperatures stabilizes the austenite phase and pushes T_{Ms} to lower temperatures. The deviation from the linear trend between 773 K and 673 K indicates that the austenite undergoes a transition from athermal martensite to isothermal martensite and is easily undercooled. This is also evident in the suppressed T_{Ms} for the 673 K sample under -80 MPa. The stress induced martensitic transformation in this strain glass is analogous to stress induced crystallization in amorphous glasses. The sudden increase in T_{Ms} for heat treatments very close to 673 K shows the complex response of the metastable austenite in the gold colored phase field. The T^* transition determined from DMA falls along the linearly extrapolated T_{Ms} curve which strongly indicates that T^* is where the austenite becomes supercooled into an unfrozen strain glass. It is believed that the defects responsible for the anisotropic, or strain, glass are vacancies, anti-site defects and the L2_1 morphology shown in Figure 8. Similar defect structures are expected to cause the mirrored exponential decrease and increase in T_{Ms} and T_f , respectively. This is captured in the anti-site defect illustrations in Figure 1B and 1C.

4.5 Thermodynamic Arrest

The three external fields (stress, magnetic field and temperature) necessary to stabilize the phase transformation were used to determine the thermodynamic arrest temperature, T_K . Although they occur close to one another, T_g and T_K should not be co-dependent in the present alloys. Indications of T_K around 150 K have been observed in the $\frac{dH_0}{dT}$ response of MSMA's that do not undergo a strain glass transition [29, 31, 37, 44]. It has been reasoned that entropy change

and resulting thermodynamic arrest in MSMA's could originate from magnetic contributions [45]. This may explain why T_f trends toward T_K between the 773K and 673K heat treatments, but further testing is required to elucidate any connections between the super spin glass and the observation of a Kauzmann point.

Recently, experiments on $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.5}\text{In}_{13.5}$ suggests that no collapse in the entropy difference between austenite and martensite can be observed above 0K [46]. Unfortunately, the entropy calculations presented in [46] compare thermodynamically inequivalent heat capacity measurements between super spin glass martensite under 0T and ferromagnetic austenite under 3T. The magnetic contribution to the austenite and martensite entropies is significant and care must be taken when calculating equilibrium conditions. As mentioned in the results section, calculating H_0 using the H_{Ms} and H_{Af} average technique is rate independent in NiCoMnIn when comparing magnetic fields ramped at 0.005 Ts^{-1} and pulsed at 5000 Ts^{-1} [36]. The austenite-martensite equilibrium was determined at thermodynamically equivalent magnetic, temperature and stress conditions. This experiment leads us to believe the observation of the Kauzmann point is not an experimental anomaly. Due to the uncertainty involved in the present experiments, T_K may fall between 80K and 150 K. This indicates that the material undergoes a T^* transition to supercooled austenite, i.e. an unfrozen strain glass, well above T_K but magnetic contributions may force the T_K transition before T_g can be reached. Further testing is required to clarify this complex competition between kinetic and thermodynamic phenomena.

5. Summary and Conclusions

To conclude, in this work it has been shown how the control of B2/L2₁ ordering can lead to the onset of strain and magnetic glass transitions in a single Ni-Co-Mn-In off-stoichiometric Heusler alloy composition. We show that with simple heat treatments that ultimately result in different fractions of L2₁ vs B2 ordering in the microstructure, it is possible to control the onset of four solid-solid phase transitions (paramagnetic-ferromagnetic, austenite-martensite, strain and magnetic glasses). The observed dynamical behavior of the strain and spin glass states of the alloy are consistent with the dynamics expected from glassy phases. Interestingly, the coupling between magnetic and strain degrees of freedom enabled us to observe a Kauzmann point where the entropy difference between martensite and austenite collapse. These materials provide an

excellent model for studying this phenomenon as direct observation of the Kauzmann point is extremely rare in glassy systems. Future work on these types of multi-ferroic glass forming systems should focus on identifying the defect structures responsible for the glassy behavior in these materials in order to allow suppression or enhancement of this glassiness via compositional variations and thermal treatments. Mapping the dependence of the Kauzmann point²s dependence on the three intensive variables; temperature, stress and magnetic field, should also be investigated. These endeavors would bring greater insights into the nature of ferroic glass transitions in particular and general glassy phases in general.

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Figures:

Figure 1. Schematic representations showing similarities between (A) structural glasses, (B) strain glasses and (C) cluster spin glasses. Critical temperatures include melting (T_m); martensite start (T_{Ms}) and Curie (T_C) phase transitions, super cooling (T^*), structural and strain glass transitions (T_g), cluster spin glass freezing (T_f) and Kauzmann (T_K).

Figure 2. A pressure vs temperature schematic for He III or IV displaying the thermodynamic scheme used to determine a Kauzmann point adapted from [20].

Figure 4. The storage modulus (E') vs temperature showing a frequency dependent second order transition at $T^* = 261$ K. The inset shows a Vogel-Fulcher-Tamman type relationship in the characteristic relaxation time (τ_0) obtained from frequency dependent modulus measurements at four temperatures.

Figure 3. Magnetization vs. temperature experiments for the 873K – 3hr – WQ sample displaying A) DC field heating after zero-field cooling and field cooling with inflections showing the Curie (T_c), martensitic transformation (T_{M_s} , T_{M_f} , T_{A_s} and T_{A_f}) and path dependent cluster spin glass freezing (T_f) temperatures and B) the real part of the AC magnetization across T_f showing a cluster spin glass frequency dependent peak shift between 1Hz and 1000Hz.

Figure 5. Magnetization (solid) and strain (dashed) measurements vs applied magnetic field for a [100] oriented single crystal in the 673 K – 3hr – WQ condition. Critical transformation austenite finish (H_{Af}) and martensite start (H_{Ms}) magnetic fields are determined using the slope intercept method.

Figure 6. Martensite start (H_{M_s}), austenite finish (H_{A_f}) and equilibrium (H_0) transformation magnetic fields vs. temperature data under -80 MPa stress that show a Kauzmann point at $T_K = 80 \text{ K}$. Two lines for each transformation magnetic fields are the results from the strain and magnetization measurements shown in Figure 5, the fact that they match quite well, indicating the high fidelity of the measurements.

Figure 7. Unit cells for (A) B2 ordering and (B) L2₁ ordering observed in NiCoMnIn Heusler alloys.

Figure 8. Dark field TEM using the (111) $L2_1$ superlattice reflection for the 673 K, 773 K, 873 K, 973 K, 1073 K and 1173 K heat treated samples.

Figure 9. Phase diagram showing the secondary heat treatment influence on the Curie (T_C), martensite start (T_{M_s}), spin glass freezing (T_f), supercooled austenite (T^*), strain glass freezing (T_g) and Kauzmann (T_K) temperatures.

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Simple heat treatments in the $Ni_{45}Co_5Mn_{36.6}In_{13.4}$ magnetic shape memory alloy leads to the observation of multiple first and second order phase transitions including strain and magnetic glassy states through change in the degree of configurational order. Phase diagram showing the heat treatment influence on the Curie (T_C), martensite start (T_{Ms}), spin glass freezing (T_f), supercooled austenite (T^*), strain glass freezing (T_g) and Kauzmann (T_K) temperatures.