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Hysteresis of magnetostructural transitions: Repeatable and non-repeatable processes

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ABSTRACT

The $Gd_5Ge_2Si_2$ alloy and the off-stoichiometric $Ni_{50}Mn_{35}In_{15}$ Heusler alloy belong to a special class of metallic materials that exhibit first-order magnetostructural transitions near room temperature. The magnetic properties of this class of materials have been extensively studied due to their interesting magnetic behavior and their potential for a number of technological applications such as refrigerants for near-room-temperature magnetic refrigeration. The thermally driven first-order transitions in these materials can be field-induced in the reverse order by applying a strong enough field. The field-induced transitions are typically accompanied by the presence of large magnetic hysteresis, the characteristics of which are a complicated function of temperature, field, and magneto-thermal history. In this study we show that the virgin curve, the major loop, and sequentially measured MH loops are the results of both repeatable and non-repeatable processes, in which the starting magnetostructural state, prior to the cycling of field, plays a major role. Using the $Gd_5Ge_2Si_2$ and $Ni_{50}Mn_{35}In_{15}$ alloys, as model materials, we show that a starting single phase state results in fully repeatable processes and large magnetic hysteresis, whereas a mixed phase starting state results in non-repeatable processes and smaller hysteresis.

1. Introduction

$Gd_5Ge_2Si_2$, $Ni_{50}Mn_{35}In_{15}$, MnAsSb, La(Fe,Si)$_{13}$, FeRh, and related alloys belong to the special class of functional materials displaying thermally induced first-order magnetostructural transitions close to room temperature [1–7]. Magnetostructural transition is the conversion process of a material from one phase to another phase structure, with the attendant change in the magnetic state [8]. For example, in the course of the thermally driven magnetostructural transition, the $Gd_5Ge_2Si_2$ alloy is converted from the orthorhombic ferromagnetic structure to the monoclinic paramagnetic structure [9,10]. However, within relatively narrow temperature ranges, the thermally driven magnetostructural transitions in this material and in similar materials can be field-induced in their reverse order by the application of a strong enough external field. As expected, the field-induced transitions give rise to sharp changes in the magnetization. For each of these materials, the temperature range where the field-induced transition occurs has been referred to as “the metamagnetic transition region”. The metamagnetic region can be defined either as the region of “phase coexistence” (i.e., region of mixed phases) or as the region where the material displays a large increase in its magnetization (as for example, the large increase in the magnetization observed when transitioning from a paramagnetic to a ferromagnetic state or from a antiferromagnetic to a ferromagnetic, as it is the case for the FeRh alloy) [11–13]. The details of the field-induced phase transitions and degree of repeatability, taking place during field cycling, is a complicated function of a number of variables, the most important of which are temperature, field, and magneto-thermal history. Gaining a better understanding of the complex interplay of these variables on the field-induced transitions and the degree of which they determine the characteristics of the MH loops during field cycling is of fundamental importance. This is because the metamagnetic region is where these materials display their attractive functional properties, e.g., large magnetocaloric effect (MCE) peaks, large magnetoresistance and magnetostriction and shape memory effects [14–18]. The display of these interesting functional properties, resulting from complicated magnetostructural changes and their potential use in different technological applications (e.g., the use of large MCE peaks for magnetic refrigeration applications) have been the main drivers for the large number of magnetic and structural studies that have been conducted on this class of functional materials during past fifteen years [14–18].

For applied fields above some threshold value in the metamagnetic region, the functional properties of these first-order materials are typically accompanied by the presence of large magnetic hysteresis. Their simultaneous occurrence, suggest that the field-induced transition processes are the mechanisms responsible for

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both the functional properties and the accompanying magnetic hysteresis.

Using magnetic data measured on $Ni_{50}Mn_{35}In_{15}$ and $Gd_5Ge_2Si_2$, in this study it will be shown that (1) magnetic hysteresis is the result of field-induced magnetostructural transitions, occurring in the metamagnetic region and (2) its repeatability or lack thereof is directly related to repeatable and non-repeatable processes taking place within the material sample during the cycling of the field. From this it follows that the results we present in this paper will provide useful insight on how to better account for magnetic hysteresis when the functional properties of the above materials are used in a cyclic manner, as for example, in magnetic refrigeration applications.

2. Material and methods

The polycrystalline $Gd_5Ge_2Si_2$ and $Ni_{50}Mn_{35}In_{15}$ alloys used in this study were both prepared by arc melting appropriate amounts of the component elements, using a water-cooled copper hearth in a high-purity argon atmosphere under ambient pressure. The purities of the alloys' component elements were better than 99.99%. The alloy ingots were turned over and re-melted several times to ensure homogeneity. The ingot of the $Ni_{50}Mn_{35}In_{15}$ alloy was annealed for 2 h at 800 °C in an evacuated quartz tube and then quenched in ice water, whereas that of $Gd_5Ge_2Si_2$ alloy was annealed in vacuum at 1300 °C for 1 h and then furnace cooled to room temperature. The chemical composition and phase structure of each alloy were determined by Energy Dispersive Spectroscopy (EDS) and X-ray diffraction analysis, respectively. The EDS chemical analysis showed that the compositions of both alloys were within 1% atom fraction of their respective target values. The magnetization of each sample alloy was measured as functions of temperature and magnetic field using a superconducting quantum interference device (SQUID) magnetometer. The zero field cooled (M_{ZFC} vs. T) plots on each material sample, were obtained by first cooling the sample at zero field down to the lowest temperature (5 K) and then applying a constant field and measuring the resulting magnetization on warming, whereas the field cooled (M_{FC} vs. T) plots were measured sequentially, following the M_{ZFC} vs. T plots, while cooling the sample under the same constant field.

3. Results

3.1. $Ni_{50}Mn_{35}In_{15}$

We have previously reported on the X-diffraction data between 273 K and 388 K obtained on the $Ni_{50}Mn_{35}In_{15}$ alloy [19]. Briefly, the X-ray data at room temperature (298 K) revealed a primary austenite phase with some amount of the martensitic phase being also present, with this latter phase being present, in diminishing amounts, up to 363 K. Cooling the alloy sample below room temperature resulted in a near disappearance of the austenite phase around 273 K. Thus, the X-ray data indicated the coexistence of the austenite and martensitic phases between 273 K and 363 K temperature range.

The M_{ZFC} and M_{FC} vs. T plots measured at a constant field of 4 kA/m (50 Oe) are shown in Fig. 1. The metamagnetic transition region, roughly extending between 250 K and 285 K, is color highlighted in the figure. In Fig. 2 are respectively shown (A) the magnetic entropy change, ΔS_M, as a function of temperature for a field change, ΔH=4000 kA/m (5 T) and (B) the first quadrant M vs. H isothermal loops measured on the same alloy sample on increasing temperature between 265 K and 290 K, at 5 K intervals. The ΔS_M vs. T plot was calculated from M vs. H isothermal data.

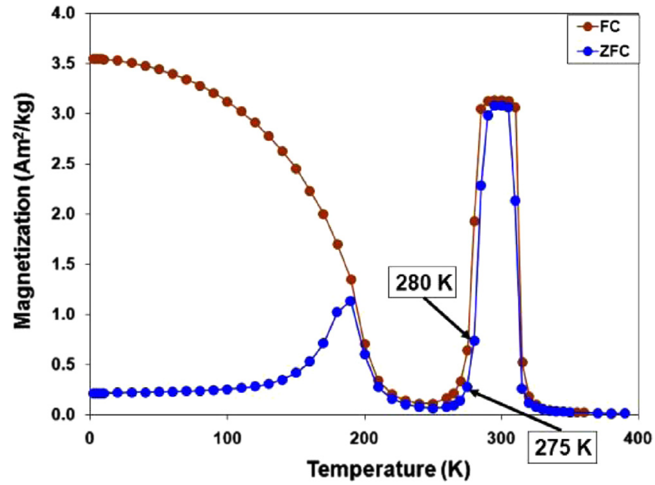

Fig. 1. M_{ZFC} and M_{FC} vs. T plots for the $Ni_{50}Mn_{35}In_{15}$ alloy measured under an applied field of 4 kA/m (50 Oe).

The ΔS_M vs. T plot shows the presence of an inverse MCE peak, roughly centered at 275 K, followed by a conventional MCE peak, whose center appears to be around 320 K. The M vs. H major loop measured at 280 K is shown in Fig. 3. Before measuring the major loop, the sample was first demagnetized, by cooling it from 300 K down to 250 K and then warming it to 280 K, all under zero field. This same demagnetizing procedure was used in measuring all the other M vs. H loops of $Ni_{50}Mn_{35}In_{15}$, with the exception of one of the loops for which a different demagnetizing procedure used; this procedure will be described later. The major loop shown in Fig. 3 reveals negligible remanence and coercivity together with the characteristics of a wasp-waist hysteresis loop, where the width of the loop is narrower near zero-field and wider at higher fields [17,18]. This behavior usually arises from the interactions of two magnetic phases. In addition, the major loop displays point-wise symmetry about the origin. Between ~250 K and ~285 K, the alloy undergoes a thermal-driven first-order transition from a low magnetization phase to a high magnetization phase. Consequently, at 280 K the sample is in a mixed magnetic state, consisting of a majority low magnetization phase with a high magnetization minority phase.

The virgin curve and the descending segment back to zero field, both measured at 280 K, are shown in Fig. 4. Two additional first-quadrant M vs. H loops, measured sequentially after measuring the virgin and descending curves are also shown in Fig. 4. The combination of the virgin curve and the descending segment is referred to as the first loop, MH loop #1, while the other two sequentially measured loops are respectively referred as the second, MH loop #2, and third, MH loop #3. The key features of these three loops can be summarized as follows. First, the virgin curve lies completely outside the major loop; secondly, the descending segments of the three loops are all identical; and, thirdly, the second and third loops are identical and also identical to the major loop (refer to Fig. 3).

In addition to a first loop similar to that shown in Fig. 4, another first loop is shown in Fig. 5. This latter loop was also measured at 280 K, except that the sample was demagnetized by first cooling it from 300 K down to 280 K. That is, skipping the step of going first to 250 K and then raising the temperature to 280 K. It is clear that these two first loops (MH loops #1) are markedly different. Specifically, the virgin curves of the two loops are different whereas the corresponding descending segments are identical. The difference between the these loops, resulted in the size of the two hysteresis loops being different, the smaller size