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Ferri- to ferro-magnetic transition in the martensitic phase of a Heusler alloy

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ABSTRACT

During the past decade the magnetic properties of Heusler alloys have been extensively studied, motivated in part by the observation of large magnetocaloric effects (MCEs) displayed by these alloys near room temperature. We present new data and develop a consistent mechanism to explain the complex hysteretic behavior of a $Ni_{50}Mn_{35}In_{15}$ Heusler alloy. The magnetization of this alloy is characterized by two critical temperatures. Below the lower critical temperature, the alloy is a *ferrimagnetic* martensite. Between the two critical temperatures, the alloy is a *ferromagnetic* martensite. Above the higher critical temperature, it is a *paramagnetic* austenite. The transitions at both critical temperatures are first order. The ferri-to-ferromagnetic transition and the crystallographic martensite-to-austenite transition explain the various facets observed in the M_{ZFC} and M_{FC} vs. T plots and their variations with increasing magnetic field. The model successfully explains the isothermal M vs. H loops near room temperature, whose behavior is strongly dependent on the initial magnetic state.

1. Introduction

The magnetic properties of Heusler shape memory alloys have been the subject of many studies. These studies have been motivated in part by the observation of large magnetocaloric effect (MCE) peaks displayed by these [1–6] and related [7–9] alloys near-room temperature. The structure and magnetic properties of the stoichiometric $Ni_{50}Mn_{25}Ga_{25}$ alloy have been of particular interest to a number of research groups. They concluded that this alloy, on heating, undergoes a first-order magnetocrystalline transition from tetragonal martensite to a cubic austenite structure at a transformation temperature, T_M, ranging from 175 K to 220 K; followed by a second-order ferromagnetic–paramagnetic transition identified with a Curie temperature of the austenite phase, T_C, between 375 K and 380 K; the transitions are reversible with temperature [10,11]. Later it was found [12–16] that the supposed transition temperatures, T_M and T_C, could made nearly coincident either by doping the alloy with Co or Cu or by slightly varying the alloy composition in the off-stoichiometric form of $Ni_{50+X}Mn_{25-X-Y}Ga_{25+Y}$, with $X \approx 5$ and $Y \approx$ l–2. The isothermal magnetization versus field loops displayed large hysteresis losses and the magnetization characteristics indicative of a field-induced magneto-structural phase transformation [17–22].

More recently, the structure and the magnetic properties of the off-stoichiometric Heusler alloy and related alloys have generated much interest because their unusual and complex magnetic properties [23–28], including the presence of a larger inverse magnetocaloric effect (MCE) peak [29] and a smaller conventional peak both occurring near room temperature as well as the display of large magnetoresistance at moderate field values [30]. Similar to what had been previously proposed for the Co or Cu-doped $Ni_{50}Mn_{25}Ga_{25}$ and the off-stoichiometric $Ni_{50}Mn_{25}Ga_{25}$ alloys, the presence of the inverse and conventional MCE peaks observed in the $Ni_{50}Mn_{35}In_{15}$ alloy is believed to be the result of the near-coincidence of two transformation temperatures both close to room temperature. That is, on heating, the Ni50Mn$_{35}$In$_{15}$ alloy has been assumed to undergo a first-order magneto-structural martensitic transformation from tetragonal martensite to ferromagnetic cubic austenite at T_M, followed by the ferromagnetic-to-paramagnetic second-order magnetic transition of the austenite phase at its Curie temperature, T_C [29–33].

The data presented by [34] is more appropriately interpreted (on heating) as a first order ferri-to-ferro-magnetic phase transition within the martensitic phase, followed by a magneto-structural transition from a martensitic to an austenitic phase at which the material becomes paramagnetic. The more recent studies by Bhobe et al. [35,36] on the phase structure and magnetic properties of the $Ni_{50}Mn_{35}In_{15}$ alloy by X-ray absorption fine structure (EXAFS) and SQUID magnetometry measurements seems to confirm that this alloy displays a cubic austenite B2 structure above 305 K and a tetragonal *L21* martensite structure below 302 K. The $Ni_{50}Mn_{35}In_{15}$

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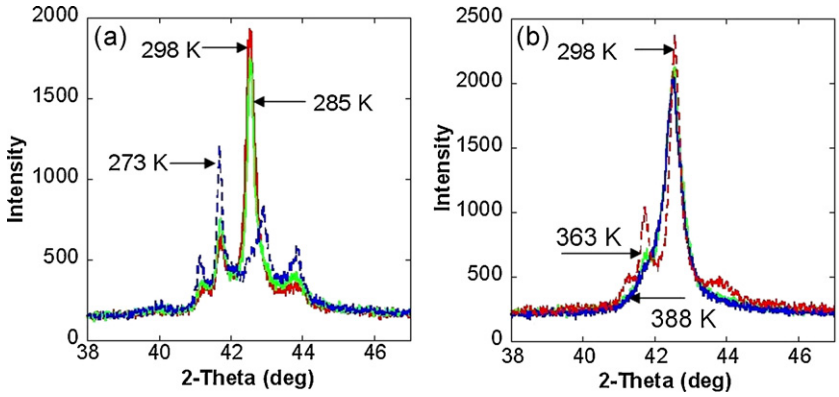

Fig. 1. X-ray diffraction patterns for the $Ni_{50}Mn_{35}In_{15}$ alloy recorded (a) on heating from 273 K to 298 K and (b) from 298 K to 388 K.

alloy undergoes a crystallographic phase transition, the details of which are affected by minute differences in the alloy composition, sample preparation, and heat treatment; however, the assumed near coincidence of T_M and T_C temperatures does not adequately account for the details of the complex magnetic behavior observed in this alloy as a function of both temperature and field. In this paper we present new magnetic data and provide a new a mechanism that accounts for the various features of this complex behavior.

2. Experimental methods

The $Ni_{50}Mn_{35}In_{15}$ alloy samples used for this study were prepared by arc melting appropriate amounts of the component elements using a water-cooled copper hearth in an argon atmosphere under ambient pressure. The sample was then homogenized for 2 h at 800 °C in an evacuated quartz tube and then quenched in ice water.

The microstructure, chemical composition, and phase structure of the alloy were then examined by energy dispersive spectroscopy (EDS), and X-ray diffraction, respectively. The EDS chemical analysis showed that the alloy composition was within 1% atom fraction of the target value of $Ni_{50}Mn_{35}In_{15}$. The magnetization data as a function of temperature at constant field values and as a function of field at constant temperatures were measured using a SQUID magnetometer.

3. Results and discussion

Fig. 1 is a summary of the X-diffraction data obtained on the $Ni_{50}Mn_{35}In_{15}$ alloy between 273 K and 388 K. The room temperature (298 K) data reveal a primary austenite phase with some amount of the martensite phase (Fig. 1a and b). The martensite phase persists in the sample on heating at least up to 363 K (Fig. 1b), whereas cooling the sample below room temperature results in the near disappearance of the austenite phase around 273 K (Fig. 1a). Therefore, the X-ray data presented in Fig. 1 clearly indicate the coexistence of the austenite and martensite phases in the temperature range from 273 K to 363 K. The details and significance of these mixed phase assemblages will be discussed elsewhere.

Fig. 2a shows the temperature dependence of the magnetization between 2 K and 390 K, measured on heating (M_{ZFC}), after the sample had been cooled in zero field from room temperature down to 2 K, and on cooling (M_{FC}) under an applied field of 4 kA/m (50 Oe) (Fig. 2a). The M_{ZFC} exhibits a rapid increase in the magnetization from ≈270 K to ≈285 K followed by a subsequent rapid decrease from ≈310 K to ≈320 K. The same M_{ZFC} plot shows also the presence of a peak at a lower temperature ($T_G \approx 190$ K), recognized as a spin glass peak. The corresponding M_{FC} vs. T plot at 4 kA/m and the M_{ZFC} and M_{FC} vs. T plots at higher field (Fig. 2b) that are presented and discussed in the following paragraphs provide additional evidence that the peak at ≈190 K is a spin glass peak.

The following observations can be made regarding the spin glass peak: (1) the center of the peak (T_G) shifts from 190 K to 160 K as the field is increased from 4 kA/m to 40 kA/m; and, as mentioned above, (2) the peak disappears for fields larger than 80 kA/m and is not present in the M_{FC} plots; (3) the magnetization values of the corresponding M_{FC} plot are somewhat higher than those of the M_{ZFC} plot from about 250 K down to T_G, below which the M_{ZFC} and M_{FC} plots begin to diverge, with M_{FC} monotonically increasing and M_{ZFC} monotonically decreasing; and (4) the decrease of T_G with increasing field, H, follows an H^{62} fit. This is close to the de Almeida–Thouless 2/3 power law that applies to spin glasses.

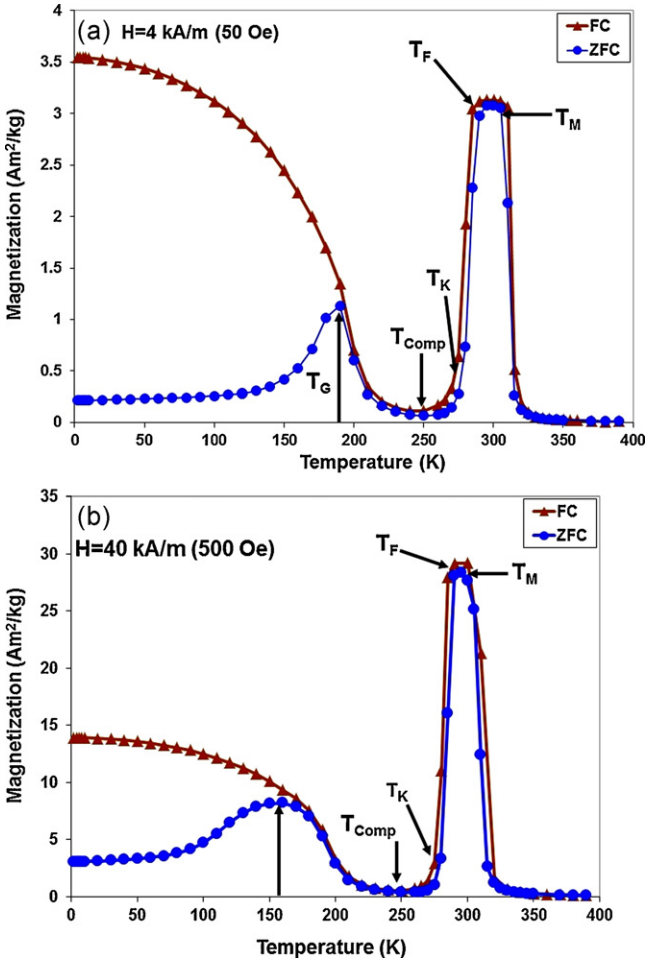

Fig. 2. M_{ZFC} and M_{FC} vs. T plots for the $Ni_{50}Mn_{35}In_{15}$ alloy measured under an applied field of (a) 4 kA/m (50 Oe) and of (b) 40 kA/m (500 Oe). The experimental uncertainty of the magnetic data is indicated by the size of the symbols in the M vs. T plots. The same uncertainty applies to magnetic data presented in Figs. 3 and 4.