

Structural and Magnetic Phase Transitions in Ni–Mn–Ga Ferromagnetic Shape-Memory Crystals

S.-Y. Chu, R. Gallagher, M. De Graef, and M. E. McHenry

Abstract—We detail crystal growth and characterization of Ni–Mn–Ga ferromagnetic shape-memory alloys (FSMA). Structural characterization includes x-ray Laue diffraction and x-ray diffraction (XRD) using θ - 2θ scans. Differential scanning calorimetry (DSC) and DC magnetization measurements have been used to probe structural and magnetic phase transformations in these materials. For the first time, the temperature dependence of magnetic torque reveals a variation of the magnetic anisotropy in stoichiometric Ni₂MnGa crystals. We also report on the effect of post-annealing on the martensitic phase transition (MPT) temperature. A Ni_{52.7}Mn_{22.6}Ga_{24.7} crystal exhibits an onset of the transformation at 304 K. The temperature hysteresis during a heating-cooling process and the full width of the transition are observed to be 2 and 10 K, respectively, for this crystal.

I. INTRODUCTION

THERE IS recent intense interest in the development of actuator materials capable of large strains, appreciable thrust, and rapid response time. Some representatives of the Heusler alloy family exhibit a cubic to tetragonal martensitic phase transformation. Since this transformation can occur between two ferromagnetic states, and involves large strains, these materials belong to a class called ferromagnetic shape memory alloys (FSMA) [1]. Unlike other magnetostrictive materials (e.g., Terfenol-D), [2] which derive their magnetostrictive strains from large magnetoelastic coupling coefficients, FSMA have vanishing elastic compliance upon approaching the MPT temperature and correspondingly large strains. From both an application and a theoretical point of view, it is necessary to determine the main physical parameters of this alloy and to estimate the influence of magnetic field and temperature on the structural and magnetic phase transition.

The temperature of ferromagnetic (T_C) and structural (T_A) phase transitions of the FSMA can be characterized by anomalies in the temperature and/or field dependence of its properties. Such properties include sample dimensions, magnetization, resistivity, enthalpy and magnetocrystalline anisotropy energy [3]–[9]. It is well known that when ferromagnetic materials undergo a symmetry lowering structural phase transformation, the crystallographic orientation of the magnetization vectors within the domains displays a corresponding change. However, such observations have not been

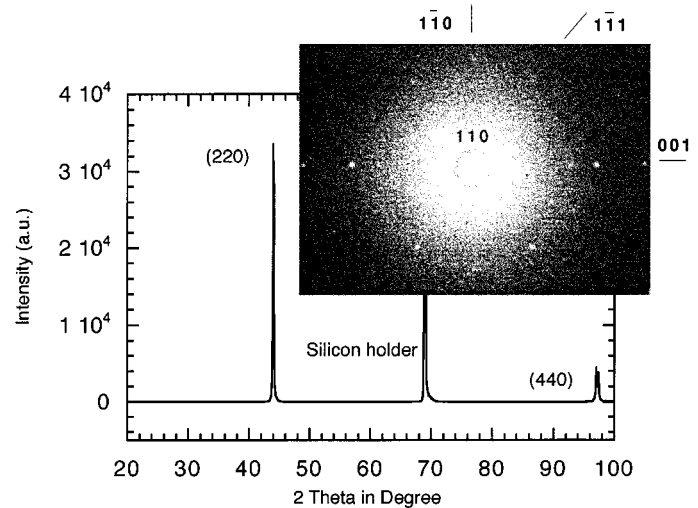


Fig. 1. Back-reflection laue x-ray photograph and an x-ray diffraction pattern with the θ - 2θ scan on the circular face of the post-annealed single crystal of Ni₂MnGa with a disk shape.

fully explored in Ni–Mn–Ga FSMA. In this paper, we use thermodynamic and magnetic measurements to study the phase transitions in stoichiometric and off-stoichiometric Ni–Mn–Ga single crystals, respectively.

II. EXPERIMENTS

Preparation of as-grown crystals with stoichiometric composition has been detailed in our previous work [9]. The single crystal studied here was cut along (110) plane from a large as-grown crystal grain. After post-annealing at 850 °C for 2 days and slowly cooling to room temperature in vacuum the single crystal was polished into a disk shape (mass = 1.10 mg, thickness = 0.17 mm, diameter = 1.01 mm). A back-reflection Laue x-ray photograph and a x-ray diffraction pattern using a θ - 2θ scan were obtained from both sides of the disk sample. As shown in Fig. 1, the circular face of the sample was aligned parallel to the (110) plane of the parent cubic $L2_1$ structure. Crystals with off-stoichiometric composition used were cut from an ingot with large crystalline grains. The ingot was grown by melting a powder mixture of the pure elements and Ni–Mn alloys in an alumina (Al₂O₃) crucible that was sealed in an evacuated quartz tube. Energy dispersive analysis in a Philips XL30 scanning electron microscope determined the composition to be Ni_{52.7}Mn_{22.6}Ga_{24.7} (at.%).

A superconducting quantum interference device (SQUID) magnetometer was used to measure the DC magnetization for both samples as a function of magnetic field and temperature. The thermodynamic properties of the off-stoichiometric

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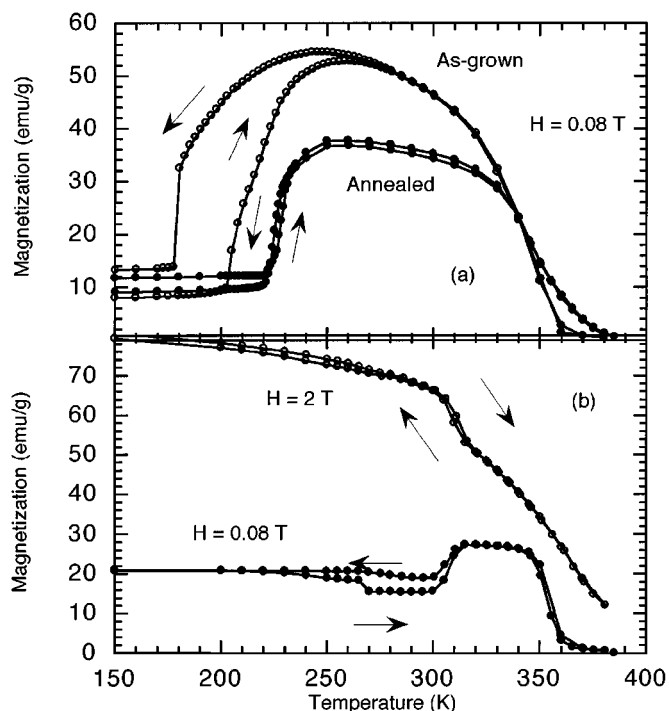


Fig. 2. Temperature dependence of the magnetization of (a) as-grown and post-annealed crystals with stoichiometric composition of Ni_2MnGa and (b) the crystals with off-stoichiometric composition of $\text{Ni}_{52.7}\text{Mn}_{22.6}\text{Ga}_{24.7}$ (at.%).

alloy were determined by differential scanning calorimetry (DSC). The DSC curves were calibrated against pure Gallium (99.999%) and Indium (99.999%) standard materials. The melting temperatures of these materials span the range of ferromagnetic and structural transitions in the FSMAs.

To determine the magnetocrystalline anisotropy energy in a stoichiometric single crystal, torque curve measurements were carried out using a Quantum Design physical properties measurement system (PPMS) with a sample rotator option. The sample was mounted on a silicon chip with a torque lever that was placed in a carrier and inserted into a superconducting solenoid. The magnetic torque ($\tau = \mathbf{m} \times \mathbf{B}$), which is created by the applied field \mathbf{B} on the sample moment \mathbf{m} , is balanced by a mechanical twisting of the torque lever. The magnetic torque is measured by a piezo-resistor in the torque lever. When the applied field, environment temperature and/or angle between the field and the sample orientation were altered, an unbalanced piezo-resistance was measured by a Wheatstone bridge connected to the piezo-resistors. Before any measurements were taken, the sample platform was calibrated by passing a current through a calibration coil built into the chip to produce a known torque in a magnetic field. In our experiments, the sample rotation axis was the [110] direction and the field was always kept in the (110) plane of the cubic parent phase.

III. RESULTS AND DISCUSSIONS

The temperature dependence of the magnetization of the as-grown and post-annealed single crystals with nearly stoichiometric composition is shown in Fig. 2(a). The following experimental protocol was employed: 1) the sample was first cooled from 385 K to 5 K in zero field; 2) then its DC magnetic

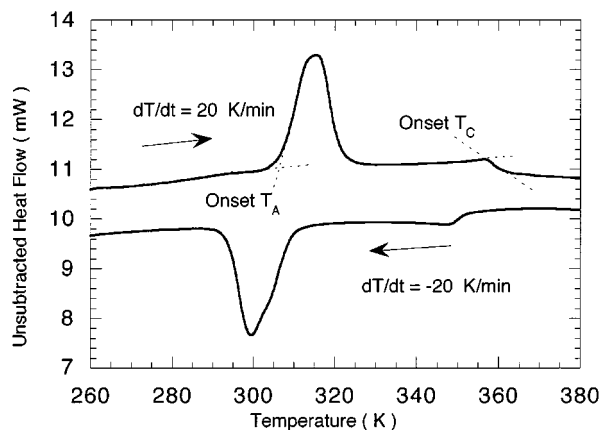


Fig. 3. Differential scanning calorimetry scans of $\text{Ni}_{52.7}\text{Mn}_{22.6}\text{Ga}_{24.7}$ (at.%) during heating and cooling.

moment was measured as a function of increasing temperature as the sample was heated above the ferromagnetic Curie temperature in applied field of 0.08 T; 3) finally the crystal was cooled to 5 K under the same applied field. In comparison with the as-grown sample, the onset temperatures of the austenite to martensite, T_M , and martensite to austenite, T_A , transitions in the post-annealed sample were significantly enhanced from 177.5 to 221.5 K and from 202.5 to 224.5 K, respectively. The post-annealing process reduced the temperature hysteresis for the structural phase transition from 25 K to less than 4 K. Meanwhile the ferromagnetic Curie temperature shifted by ~ 7 K from its original value (~ 370 K).

The post-annealing effect can be interpreted in terms of a reduction of dislocation density, compositional fluctuation and second phase in the as-grown sample. High temperature annealing made the sample more homogenous in composition and microstructure. The faults in our sample might present in a amounts less than the detection limit of x-ray diffraction, however a sharp step in a magnetization curve is a signature of a cooperative phase transition. The elimination of a possible contamination phase may result in a decrease of the magnetic coercivity because an impurity phase in a ferromagnetic material can serve as a domain wall pinning phase and increase the coercivity. A magnetic hysteresis measurement in the post-annealed sample shows its coercivity to be 50 Oe which is much smaller than the ~ 250 Oe coercivity of the as-grown sample [9].

The microstructure is not the only factor that influences the phase transition behavior. In fact, compositional changes are known to dramatically affect the ferromagnetic and structural transition temperatures [8]. We have prepared a set of Ni–Mn–Ga (Al) alloys with different T_C and T_A . As an example, an off-stoichiometric alloy of composition $\text{Ni}_{52.7}\text{Mn}_{22.6}\text{Ga}_{24.7}$ (at.%) exhibits onset temperature for the structure transition and magnetic transition at 304 K and ~ 359 K. The shape of the magnetization curves shown in Fig. 2(b) is typical of magnetization curve for occurring a structure transition in the FSMAs at low and high field.

To confirm this result, a DSC curve is shown in Fig. 3. After calibration corrections the onset temperatures of the structure transition T_A and the ferromagnetic transition T_C are

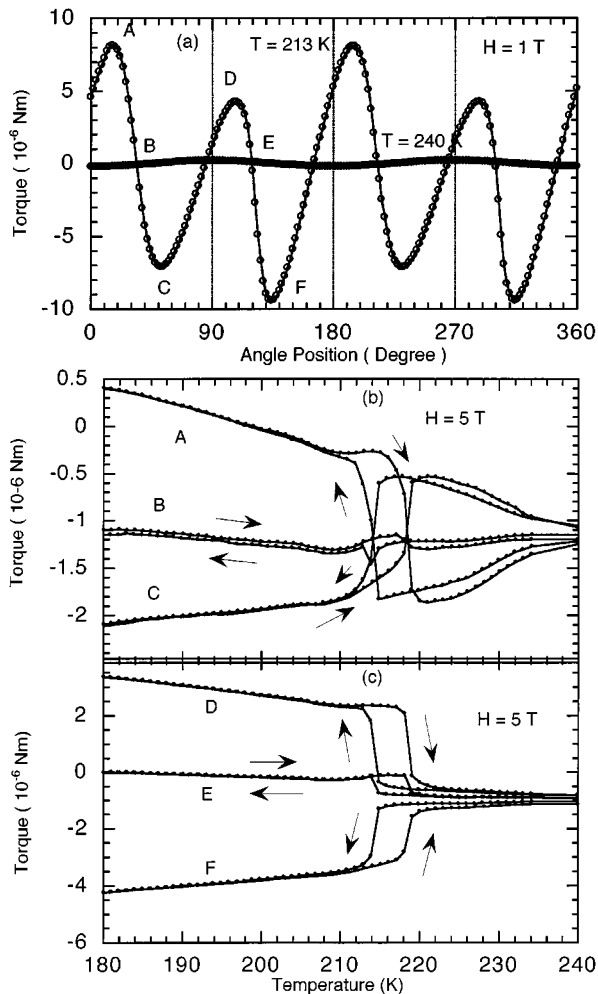


Fig. 4. (a) Angle Position, and (b) and (c) temperature dependence of magnetic torque of the post-annealing Ni_2MnGa single crystal at fields of 1 T and 5 T, respectively.

determined to be 303.0 K and 354 K, which coincide with those shown in Fig. 2(b). The temperature hysteresis as well as the enthalpy and magnetic entropy changes during the structural transition will be described in a forthcoming paper.

Spin reorientation in a stoichiometric composition sample has been investigated by a magnetic torque measurement for the first time. In Fig. 4(a), following a zero field cooling, the torque is

shown as a function of angle between the applied field (1 T) and a reference orientation. A large value from peak to peak on the torque curve implies that in comparison with the cubic structure (at 340 K) the tetragonal structure (at 213 K) exhibits a strong magnetic anisotropy.

Fig. 4(b) and (c), which show the magnetic torque curves as a function of varied fixed angle positions indicated by the letters in Fig. 3(a), provide clear evidence of microstructure transformation from the cubic to tetragonal structure. The thermal hysteresis of the structural transition at fixed positions is about 4 K. Fitting these curves may not only involve the spin reorientation in the tetragonal structure but also the distribution of the twin variants and the twin boundaries moving in the applied field. A detailed description of the crystal anisotropy energy in this ferromagnetic system will be discussed in the future.

IV. CONCLUSIONS

Post-annealing of a stoichiometric ferromagnetic shape memory alloy Ni_2MnGa can enhance the structural transition temperature and reduce the coercivity and the ferromagnetic Curie temperature. An off-stoichiometric composition $\text{Ni}_{52.7}\text{Mn}_{22.6}\text{Ga}_{24.7}$ (at.%) sample exhibits the structural transition near room temperature. DSC, DC magnetization and magnetic torque curves provide evidence of an enthalpy change, magnetization and microstructure transformation from the cubic structure to the tetragonal structure.

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