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Observation of room temperature magnetocaloric effect in $Mn_{0.9}Ni_{1.1}Ge$ alloy

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ABSTRACT

We report detailed magnetic and magnetocaloric studies of a self-doped composition $Mn_{0.9}Ni_{1.1}Ge$ in ambient as well as in high pressure situation. The alloy undergoes martensitic phase transition (MPT) around the room temperature and orders antiferromagnetically below 200 K. Room temperature structural analysis indicates clear signature of co-existing hexagonal and orthorhombic phases. Application of external hydrostatic pressure (P) results in a shift in the martensitic transition temperature towards the lower value. A significantly large magnetocaloric effect (MCE) around the MPT ($\Delta S = -6.1$ J/kg-K at 295 K and -6.11 J/kg-K at 282 K during heating and cooling respectively for H changing from $0 \rightarrow 50$ kOe) has also been observed. The magnitude of MCE is hardly affected by the application of external P.

1. Introduction

Magnetic refrigeration, a recently developed environment friendly cooling technology, is based on the magnetocaloric properties of the refrigerant materials [1–4]. Magnetocaloric effect (MCE) is defined as the adiabatic change in magnetic entropy (ΔS) (hence, adiabatic change in temperature (ΔT)) in varying magnetic field (H). During last two decades, several research works have been performed to find new and efficient magnetic refrigerants for room temperature applications [5–19]. Among various inorganic materials, magnetic equiatomic alloys (MEAs) with general formula MM′X (where M, M′ = transition metals and X = Si, Ge, Sn etc.) and their derivatives are found to be promising candidates for magnetic cooling applications (due to the presence of large MCE) [20–27]. Apart from MCE, MEAs and their derivatives show several other remarkable and applicable functional properties, such as shape memory effect, magnetoresistance, exchange bias, superelasticity etc. [25,28–34]. The diffusionless first order structural transition, called the martensitic phase transition (MPT), plays crucial role towards the observation of such diverse functional properties. In addition, recent works indicate a significant effect of hydrostatic pressure on the functional properties of these MEAs [35–41].

The stoichiometric MnNiGe alloy of MEA family undergoes MPT from high temperature hexagonal Ni_2In-type austenite state (space group: $P6_3/mmc$) to orthorhombic TiNiSi-type martensite state (space group: $Pnma$) at 470 K and orders antiferromagnetically below 346 K [42,43]. To enhance it's functionality and make it usable for room temperature application, several doping studies have been performed (self doping and foreign element doping) [21,22,25,30,43,44]. Though foreign element doping (both with larger and smaller size atoms in Mn, Ni or Ge sites) in MnNiGe alloy is a common scenario, very few works have been performed on self doping case [39,44,45]. Recently, we have investigated a self doped alloy of composition $MnNi_{0.9}Ge_{1.1}$, prepared by replacing Ni atom with Ge atom [45]. Interestingly, it shows both conventional and inverse MCE. In this alloy, the Mn-Mn inter-layer antiferromagnetic (AFM) interaction remains unaffected, whereas a decrease in lattice parameters (and hence a decrease in Mn-Mn intra-layer distance) induces ferromagnetism in otherwise AFM alloy. In the present work, our aim is to affect the Mn-Mn spiral AFM interaction by breaking Mn-Mn inter-layer chain and to bring the MPT of the alloy around room temperature [42]. For this purpose we have prepared an alloy of nominal composition $Mn_{0.9}Ni_{1.1}Ge$, where we have replaced some Mn atom with Ni atom and investigated its magnetic and magneto-functional properties in ambient as well as in presence of external hydrostatic pressure.

2. Experimental details

The polycrystalline alloy of nominal composition $Mn_{0.9}Ni_{1.1}Ge$ was prepared by melting the constituent elements (purity ⩾99.9%) using a tri-arc furnace in an inert argon atmosphere. The as-cast ingot was then annealed at 800 °C in an evacuated quartz tube for 100 h followed by rapid quenching in ice water. The room temperature X-ray powder diffraction (XRD) pattern, recorded in a Bruker AXS diffractometer (D8-Advance) using Cu-K_α radiation, indicates the presence of both Ni_2In-type hexagonal (space group: $P6_3/mmc$) and TiNiSi-type orthorhombic (space group: $Pnma$) phases in the alloy. The recorded powder

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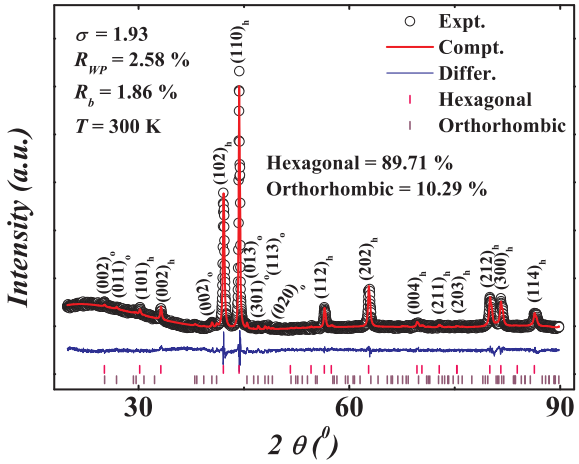

Fig. 1. Experimental (circle) and calculated (solid line; fitted by peak profile Rietveld refinement) X-ray powder diffraction pattern of $Mn_{0.9}Ni_{1.1}Ge$ compound along with Miller indexes for both hexagonal and orthorhombic phases of visible Bragg's reflection, difference pattern (residue) and peak positions at room temperature.

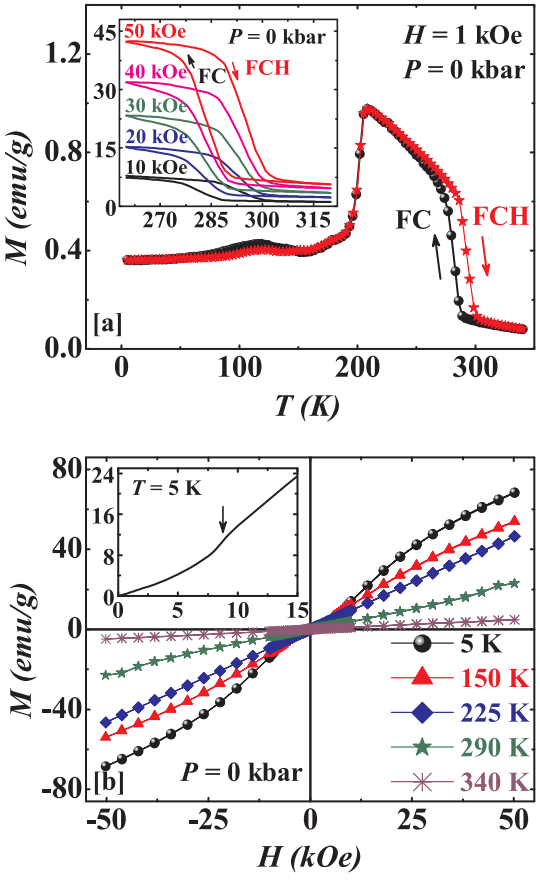

Fig. 2. (a) Depicts the temperature (T) variation of dc magnetization (M) in field-cooling (FC) and field-cooled-heating (FCH) protocols under an applied field of 1 kOe. Inset of (a) represents $M(T)$ data at different applied H in a restricted T range. (b) shows isothermal $M-H$ curves at different constant T. Low-H region of 5 K $M(H)$ curve is plotted in the inset of (b).

diffraction data was analyzed by Reitveld refinement method using MAUD software package [46]. The experimental, computed and difference patterns along with the peak positions at room temperature are plotted in Fig. 1. Low values of different refinement parameters (σ = 1.93, R_{WP} = 2.58%, R_b = 1.86%) confirm the absence of any

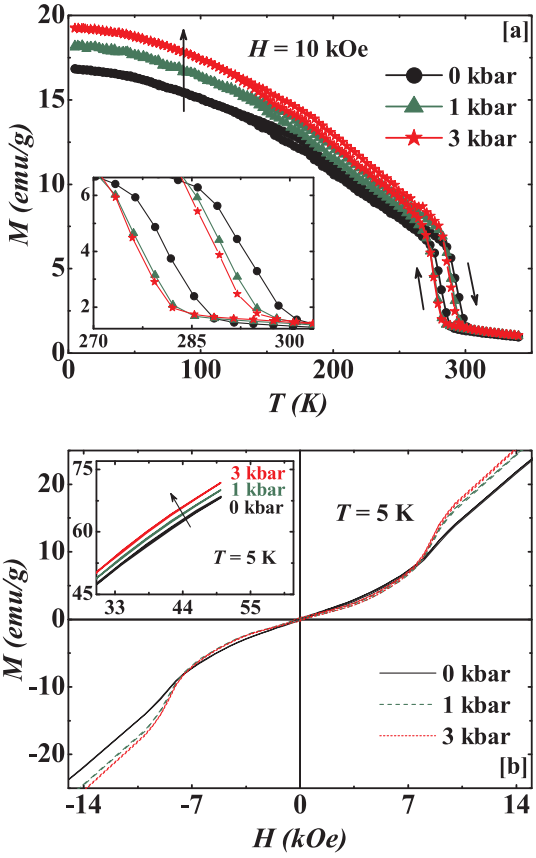

Fig. 3. The temperature (T) variation of dc magnetization (M) (both in FC and FCH protocols) recorded in presence of 10 kOe of magnetic field (H) with various applied hydrostatic pressure (P) are plotted in the main panel of (a). A restricted region of the $M(T)$ curves are shown in the inset of (a). Inset and main panel of (b) represents the restricted regions of the isothermal variation of M as a function of H at 5 K in presence of different applied P.

impurity phase in the studied alloy. Our XRD analysis also confirms the presence of 89.71% of hexagonal phase along with 10.29% of orthorhombic phase at room temperature. The lattice parameters of both the phases present in the studied alloy at room temperature are found to be a_h = 4.08 Å; c_h = 5.40 Å for hexagonal phase and a_o = 6.02 Å; b_o = 3.75 Å; c_o = 7.07 Å for orthorhombic phase. Dc magnetic measurements at ambient as well as at high pressure condition were measured using a Quantum Design SQUID magnetometer (MPMS XL 7, Evercool model). High pressure measurements were conducted using an MPMS high pressure capsule cell 8.5 with Daphne as pressure transferring medium.

3. Results and discussion

We recorded temperature (T) variation of dc magnetization (M) in field cooling (FC) and field-cooled heating (FCH) protocols under an applied field (H) of 1 kOe (see main panel of Fig. 2(a)). On cooling from 340 K, a sharp increase in dc M has been observed around 290 K. Further decrease in sample T results in a sharp decrease in M value around 200 K followed by a sluggish decrease. This drop in M value around 200 K is an indication of the onset of AFM ordering in the studied alloy. An additional anomaly in M *vs.* T data is visible around 120 K, which is due to the change in magnetic structure. Such change in magnetic structure is also present in stoichiometric MnNiGe alloy around 185 K [42]. A clear thermal hysteresis is found to be associated with the $M(T)$ data (between FC and FCH) with sharp change of M value around 300 K, indicating the first order nature of the transition. This thermal hysteresis also supports the observed phase coexistence at room