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Large refrigeration capacities near room temperature in $Ni_2Mn_{1-x}Cr_xIn$

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ABSTRACT

We report on the observation of large refrigeration capacities near room temperature in $Ni_2Mn_{1-x}Cr_xIn$ Heusler alloys. The alloys exhibit the $L2_1$ cubic crystal structure and undergo a second order ferromagnetic to paramagnetic phase transition. The respective Curie temperatures vary with Cr concentration from 315 K to 290 K. Net refrigerant capacities of up to 60 J/kg and 168 J/kg are observed in the alloys for applied magnetic fields of 20 kOe and 50 kOe, respectively. Due to the second order phase transition, the materials do not exhibit any hysteresis loss or other problems usually associated with materials exhibiting first order phase transitions. The observed refrigeration capacities in $Ni_2Mn_{1-x}Cr_xIn$ are higher than those observed in many Heusler alloys with first order magnetic transitions.

1. Introduction

The magnetocaloric effect (MCE) is a thermodynamic process where an isothermal magnetic entropy change, ΔS_M, driven by an external magnetic field yields an adiabatic change in the temperature (ΔT_{ad}) of a material. [1] The MCE phenomenon can be exploited in cooling devices that are environmental friendly and energy efficient when compared to current gas compression-based refrigeration systems. [2] The interest in magnetocaloric cooling devices and materials exhibiting giant MCE has intensified primarily due to the result of two important developments in the late 90's. First, the demonstration of a prototype near-room temperature refrigerator using metallic Gd was described by Zimm et al. [3] The second being the discovery of a giant magnetocaloric effect in $Gd_5(Si_2Ge_2)$. [4] These advances have led to intense research activities in search for materials with large MCE, and eventually giant MCE materials like $Mn(As_{1-x}Sb_x)$, [5] $MnFe(P_{1-x}As_x)$, [6] $La(Fe_{13-x}Si_x)$ [7] and several Ni-Mn-X (X=Ga, In, Sb, Sn) [8] based Heusler alloys were discovered.

In common, the giant MCE in these materials is attributed to a coupled first order magnetostructural phase transition (FOMT), where the magnetic transition in the material is accompanied by a structural phase transition. In the case of Heusler alloys, the FOMT is a martensitic phase transition (MPT) during which a structural transformation from a cubic austenite to a non-cubic martensite phase takes place. Although giant MCE (particularly large ΔS_M) is observed in the vicinity of the phase transition of FOMT materials, several problems prevent most of these materials from being applied in a practical cooling device. These FOMT materials are plagued with cracking, corrosion, and thermal/magnetic hysteretic behavior over many cycles due to the stresses of repeated structural transformation, all of which lead to a deterioration of the robust MCE properties. [9] In this regard, materials exhibiting a second order magnetic transition (SOMT), like the rare earth metal Gd, are advantageous. Although the peak ΔS_M in SOMT compounds are much lower when compared to that of FOMT materials, no hysteresis loss is observed in SOMT materials, and hence the refrigeration capacity (RC) (which is a more appropriate measure of MCE) in these materials may be relatively higher. Therefore, SOMT materials may be more practical for application in solid state cooling technologies [10].

Among the Heusler alloys exhibiting a martensitic transformation, Mn rich off-stoichiometric $Ni_2Mn_{1+x}In_{1-x}$ alloys have been extensively studied. The MPT in $Ni_2Mn_{1+x}In_{1-x}$ can be tuned over a wide range of temperatures, and therefore these materials are of great interest from a MCE perspective [11–13]. Although many reports regarding the MCE of off-stoichiometric $Ni_2Mn_{1+x}In_{1-x}$ based alloys can be found in the literature, the detailed magnetic properties (especially the MCE) of stoichiometric Ni_2MnIn has not been reported so far. The material exhibits the $L2_1$ cubic structure and is ferromagnetic with a Curie temperature, T_C, of 315 K [14].

Considering the near room temperature T_C of Ni_2MnIn, it is interesting to investigate the magnetic and magnetocaloric properties of this material. The study is also interesting in light of the recent report by Singh et al., in which they reported on the enhanced magnetocaloric properties in off-stoichiometric $Ni_2Mn_{1.4}In_{0.6}$ [15]. The material exhibits large magnetization and a corresponding large magnetic entropy change at T_C. Keeping the above discussion in mind,

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we present an experimental study on the structural and magnetic properties of the Cr doped $Ni_2Mn_{1-x}Cr_xIn$ Heusler alloy system. By Cr doping we intended to tune the T_C of the system over a wide range of temperatures while exploring the magnetocaloric properties of the system.

2. Experimental techniques

Approximately 2 g of polycrystalline $Ni_2Mn_{1-x}Cr_xIn$ ($0.0 \le x \le 0.10$) buttons were fabricated by arc melting and annealing techniques. The constituent metals, of more than 3N purity, (obtained from Alfa Aesar, Inc.) were repeatedly melted in an argon atmosphere, and the weight loss of each sample after melting was less than 0.5%. For homogeneity, the samples were annealed in partially evacuated (partially filled with Ar) vycor tubes for 72 h at 1123 K, followed by quenching in cold water. Samples for experimentation were cut from the bulk buttons using a low-speed diamond saw.

The structure and phase purity of the samples were explored by performing x-ray diffraction (XRD) measurements on a Scintag PAD-X1 Powder x-ray diffractometer, with a monochromatic Cu-Kα_1 radiation source. All XRD measurements were performed at room temperature. The crystalline structure and lattice parameters were determined using Powder Cell diffraction software [16].

The magnetization measurements were conducted on a physical property measurement system (PPMS) from Quantum Design, Inc. The measurements were performed in the temperature range of 5–400 K and in applied magnetic fields of up to 50 kOe. The magnetic entropy changes were evaluated from the isothermal magnetization as a function of applied magnetic field data at various temperatures near T_C using the Maxwell relation shown below: [17]

$$\Delta S_M = -\int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \quad (1)$$

3. Results and discussion

The room temperature XRD patterns of $Ni_2Mn_{1-x}Cr_xIn$ are shown in Fig. 1. The alloys crystallize in the $L2_1$ cubic structure belonging to the $Fm3m$ space group. With increasing Cr concentration, the lattice parameters linearly increase by 0.081% from a=6.0610 Å (x=0.0) to a=6.0659 Å (x=0.10). Assuming that Vegard's law holds (which is reasonable considering that the structure is cubic and the $Ni_2Mn_{1-x}Cr_xIn$ solid solution is nearly ideal), this suggests that the

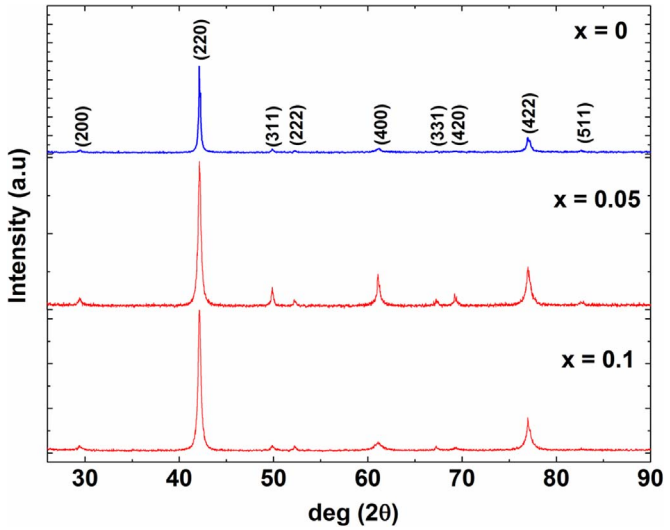

Fig. 1. Room temperature XRD patterns for $Ni_2Mn_{1-x}Cr_xIn$.

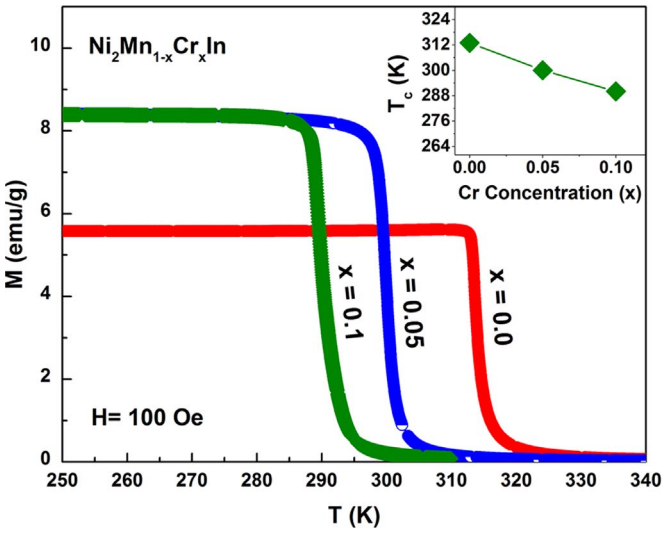

Fig. 2. Temperature dependence of dc magnetization of $Ni_2Mn_{1-x}Cr_xIn$ measured in an applied magnetic field of 100 Oe. The inset shows the dependence of T_C on the Cr concentration x.

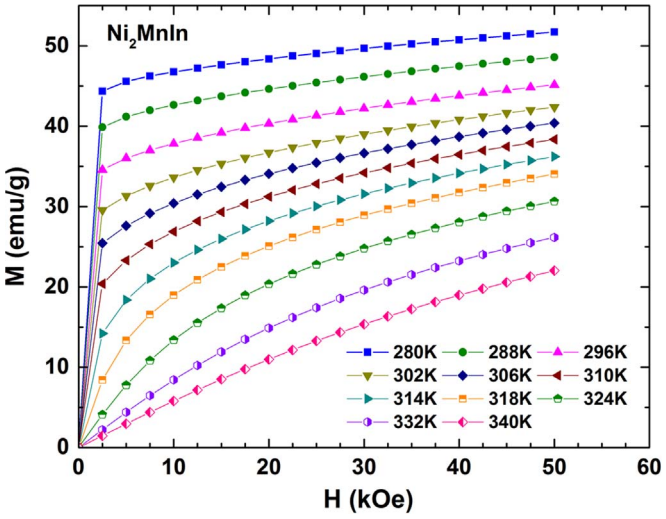

Fig. 3. Isothermal magnetization as a function of applied magnetic field of $Ni_2Mn_{1-x}Cr_xIn$ (x=0) measured at various temperatures.

stoichiometry of our samples is close to the targeted stoichiometry. The lattice parameter of Ni_2MnIn observed in this work is consistent with the literature.[12] In terms of the coordination number, CN=12, and depending on the number of electrons contributed to the conduction band when combined with other metals, Mn and Cr may have different metallic radii. For a valence of 3 and 6, the radii for Cr are 1.36 Å and 1.282 Å, respectively. The radii for Mn are 1.304 Å and 1.264 Å depending on the valence of 4 and 6, respectively. The linear increase of lattice parameter with increasing Cr concentration implies that the radius of Cr is larger than that of Mn in $Ni_2Mn_{1-x}Cr_xIn$.

Fig. 2 shows the magnetization as a function of temperature, $M(T)$, data of $Ni_2Mn_{1-x}Cr_xIn$ samples measured in a magnetic field of 100 Oe. Before each measurement, the respective sample was cooled down to 5 K in zero magnetic field. Upon the stabilization of the temperature, a 100 Oe magnetic field was applied and the $M(T)$ data was obtained as a function of increasing magnetic field. All $M(T)$ measurements were performed in temperature range of 5–350 K. For clarity, the data from 250 to 340 K are shown in Fig. 2. As shown in the figure, the magnetization of all samples remains nearly unchanged with increasing temperature until T_C, where the magnetization sharply drops to zero. This typical ferromagnetic behavior that show the ferromagnetic to