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The Effect of Fe and Ni Substitution in Magnetocaloric MnCoGe

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The MnCoGe family of compounds shows potential as a rare-earth free material for magnetocaloric applications around room temperature. We present initial findings on the effects of the substitution of Fe and Ni for Mn in a series of $Mn_{1-x}T_xCoGe$ compounds (T = Fe, Ni; x = 0.04 - 0.10). Investigations include x-ray diffraction, differential scanning calorimetry(200 - 670 K) and magnetisation (5 - 350 K) measurements in magnetic fields up to 8 T. The influence of the Fe and Ni substitutions on the transformation temperature between the hexagonal and orthorhombic structures, the resultant phase fractions and their magnetic phase transitions are reported.

1. Introduction

Materials which utilise the magnetocaloric effect (MCE) have attracted increasing attention in the past two decades due to the promise of refrigeration applications as an alternative to conventional vapour-cycle systems with the prospects of energy savings and environmentally friendly technology [1]. In particular, the work of Pecharsky and Gschneidner [2] reported in 1997 offered scope for applications around room temperature. Many systems have been explored since then including $Gd_5Ge_2Si_2$ [2], $LaFe_{11.4}Si_{1.6}$ [3] and $NdBaMn_2O_6$ [4].

MnCoGe also exhibits transitions around room temperature and, given that it comprises relatively low cost materials, systems based on MnCoGe have also attracted attention [5-7]. MnCoGe can form in two crystal structures [8]: an orthorhombic TiNiSi-type structure (space group P*nma*) with a Curie temperature T_C^{orth} = 345 K [5]; and a hexagonal Ni_2In-type structure (space group P6_3/*mmc*) with a Curie temperature T_C^{hex} = 275 K [9]. With decreasing temperature, MnCoGe shows a diffusionless transformation from the austenitic hexagonal phase to the martensitic orthorhombic phase at T_{str} ~ 650 K [10]. T_{str} can be controlled in a variety of ways including: pressure [11], introduction of substitutional [12] or interstitial atoms [13], leading to the observation of first order phase transitions (FOPT) in several MnCoGe-based systems [14-16]. For materials with a FOPT, a magnetic field can simultaneously change the magnetic and lattice entropies due to the coupling between the crystallographic structure and the magnetism and hence may exhibit a giant magnetocaloric effect (GMCE). Here, we report the initial findings of our attempt to tune the T_{str} of $Mn_{1-x}Fe_xCoGe$ and $Mn_{1-x}Ni_xCoGe$ compounds in order to create a first order phase transition.

2. Sample preparation

The polycrystalline $Mn_{1-x}Fe_xCoGe$ and $Mn_{1-x}Ni_xCoGe$ samples (x= 0.04, 0.06, 0.08, 0.10) were prepared by repeated argon-arc melting of stoichiometric amounts of 99.9% pure Mn, Co, Ge plus 99.99% Fe and Ni. The mass loss of Mn during melting was compensated by adding 3% excess Mn to the starting materials. The resulting ingots were wrapped in tantalum

foil and sealed in evacuated quartz tubes, then annealed at 850°C for five days followed by quenching in water. The samples were characterised by powder x-ray diffraction measurements at room temperature (XRD; CuKα radiation). The magnetisation was measured in magnetic fields of 0.01 T in both zero field cooling (ZFC) and field cooling (FC) modes over the temperature range from 5 K to 350 K using a Physical Properties Measurement System (Quantum Design PPMS). In addition, the field dependence of the magnetisation was measured in magnetic fields up to 8 T, from 200 K to 350 K in steps of 5 K. Several samples were also investigated by differential scanning calorimetry (DSC) measurements from 200 K to 670 K.

3. Results and Discussion

3.1 Structures; Phases

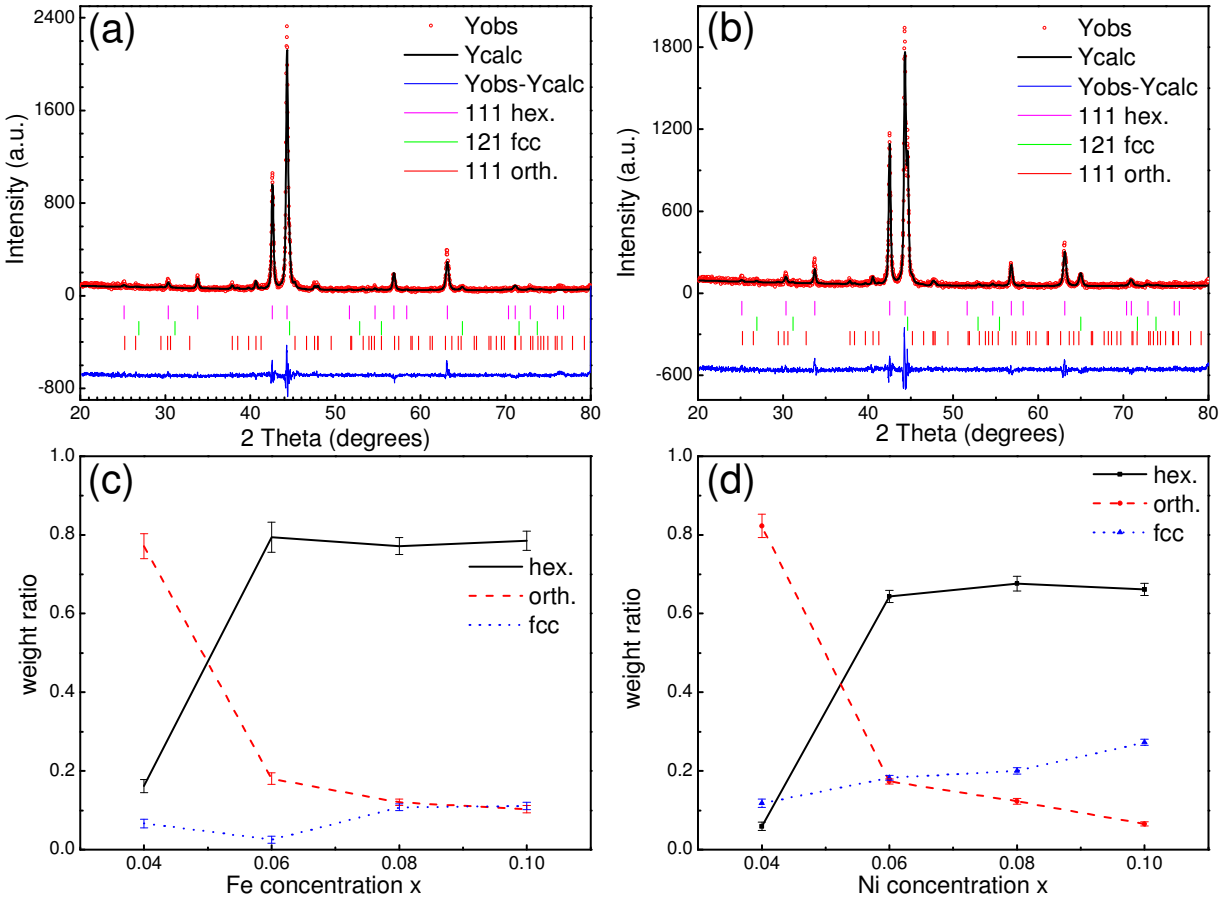

Fig. 1 X-ray diffraction patterns and Rietveld refinements (see text) for: (a) $Mn_{0.92}Fe_{0.08}CoGe$ and (b) $Mn_{0.90}Ni_{0.10}CoGe$; individual phase contents ("weight ratio") as functions of dopant concentration for: (c) $Mn_{1-x}Fe_xCoGe$ and (d) $Mn_{1-x}Ni_xCoGe$

The x-ray diffraction Rietveld refinements (using FullProf) of $Mn_{0.92}Fe_{0.08}CoGe$ and $Mn_{0.92}Ni_{0.08}CoGe$ are shown in Figs. 1(a) and 1(b) respectively with both systems found to exhibit coexistence of the hexagonal and orthorhombic phases as expected. This phenomenon indicates that the transformation temperature is around room temperature. However, an impurity phase identified as $MnCo_2Ge$ (fcc structure, space group F*m-3m*) is also observed in both systems. As shown by Figs. 1(c) and 1(d), the $MnCo_2Ge$ phase is more pronounced in $Mn_{0.90}Ni_{0.10}CoGe$ than in $Mn_{0.92}Fe_{0.08}CoGe$. The preliminary assumption is that Ni shows a

greater preference than Fe to enter into the Co site in $MnCo_2Ge$ rather than the Mn site in MnCoGe.

The fraction of the three phases identified in $Mn_{1-x}Fe_xCoGe$ and $Mn_{1-x}Ni_xCoGe$ - hexagonal, orthorhombic and $MnCo_2Ge$ - are shown as functions of Fe and Ni concentrations in Figs. 1(c) and 1(d) respectively. The hexagonal phase is found to increase with increasing Fe and Ni concentrations while the orthorhombic phase decreases. This implies that T_{str} is reduced with increasing Fe or Ni content. The fraction of the fcc $MnCo_2Ge$ phase present in the $Mn_{1-x}Fe_xCoGe$ system remains relatively low (< 11(1) %) with increases in x while the fraction of the fcc $MnCo_2Ge$ in $Mn_{1-x}Ni_xCoGe$ increases from ~ 12(1) % to ~ 27(1) %. The $MnCo_2Ge$ phase is likely to have occurred during the sample preparation process, when the arc beam encounters the raw materials, causing a dispersal of the Ge powder. The loss of Ge drives $Mn_{1-x}T_xCoGe$ towards the $MnCo_2Ge$ structure. To avoid this problem in future sample preparations, the Ge powder will first be melted to solid form.

3.2 Magnetic properties

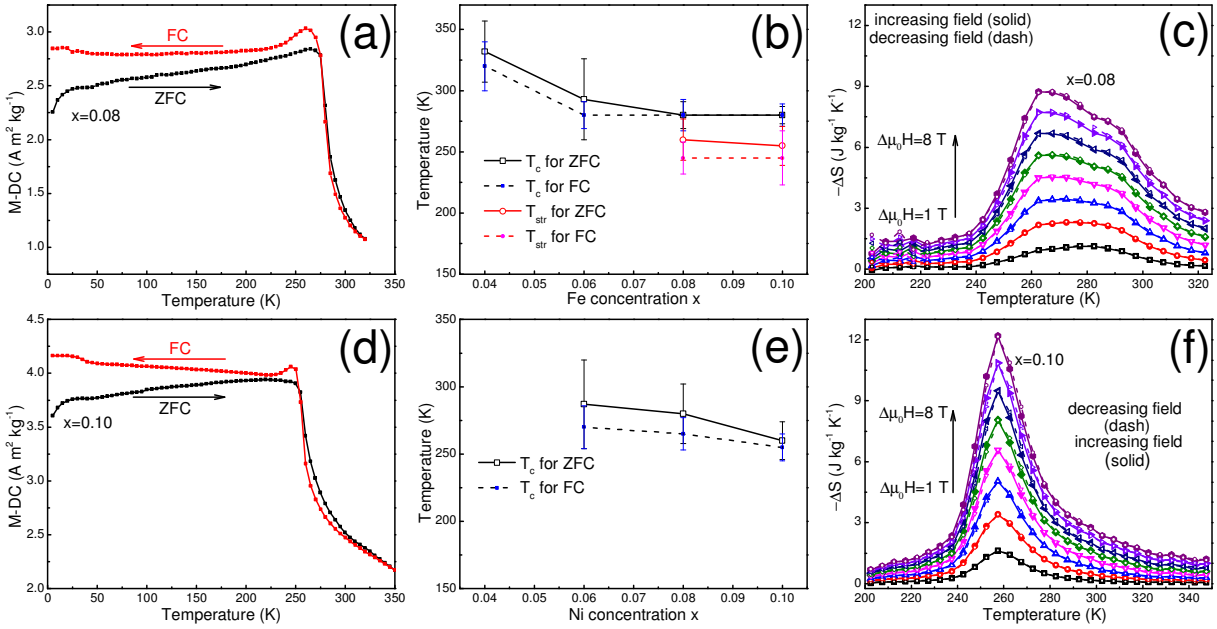

Fig. 2 Magnetic data for $Mn_{1-x}Fe_xCoGe$ ((a), (b), (c)) and $Mn_{1-x}Ni_xCoGe$ ((d), (e), (f)): (a) and (d) M-T curves (B=0.01 T); (b) and (e) transition temperatures (determined from dM/dT curves) versus Fe and Ni concentrations; (c) and (f) isothermal entropy changes. ($\Delta\mu_0H$ = 1 T to 8 T in (c) and (f); the data points are linked by straight lines as a guide to the eye.)

The magnetisation curves for $Mn_{0.92}Fe_{0.08}CoGe$ and $Mn_{0.90}Ni_{0.10}CoGe$ are shown as a function of temperature in Figs. 2(a) and 2(d). The magnetisation does not tend to zero beyond the main magnetic phase transition up to 350 K. This is attributed to the existence of the fcc phase. The transition temperatures obtained by differentiation of the M-T curves are summarized in Figs. 2(b) and 2(e). For $Mn_{1-x}Fe_xCoGe$ (x = 0.04 and 0.06) there is only one transformation. For each transformation, however, two different temperature points were obtained according to the splitting between the ZFC and the FC curves around the magnetic transition temperature, which indicates the presence of thermal hysteresis [17, 18]. In many magnetocaloric materials [2, 12, 19], such hysteresis implies the existence of FOPT due to the combination of magnetic and structural transitions. For $Mn_{1-x}Fe_xCoGe$ with x = 0.08 and 0.10 two transitions are observed up to 350 K; the transitions around 280 K most likely indicate the magnetic transition of the hexagonal phase for both samples with the lower transitions around 260 K and 255 K, respectively, being due to transformation to the orthorhombic structure. In

contrast, only one transition temperature (FOPT) is observed up to 350 K for each of the $Mn_{1-x}Ni_xCoGe$ samples.

The isothermal entropy changes -ΔS for $Mn_{0.92}Fe_{0.08}CoGe$ and $Mn_{0.90}Ni_{0.10}CoGe$ derived from the magnetisation versus field curves (T = 200 - 350 K; B = 0 - 8 T; not shown) are shown in Figs. 2(c) and 2(f) respectively. The entropy changes were calculated using the standard Maxwell function (see e.g. [20]). $Mn_{0.92}Fe_{0.08}CoGe$ exhibits two peaks in -ΔS ~ 5.6 J/kg·K at ~ 262 K and ~ 5.0 J/kg·K at ~ 283 K for ΔB = 0 - 5 T. The isothermal entropy change for $Mn_{0.90}Ni_{0.10}CoGe$ is -ΔS ~ 8.0 J/kg·K at ~258 K (ΔB = 0 - 5 T).

3.3 Differential Scanning Calorimetry

DSC curves for $Mn_{0.92}Fe_{0.08}CoGe$ and $Mn_{0.90}Ni_{0.10}CoGe$ are shown in Figs 3(a) and 3(b) respectively. Preliminary analyses (e.g. inserts to Fig. 3) indicate two transitions, ~ 292 K and ~267 K, within the range 200-350 K for $Mn_{0.92}Fe_{0.08}CoGe$, compared with ~ 270 K and ~ 250 K as indicated by the magnetic measurements (Fig. 2(b)) with a single transition ~ 258 K for $Mn_{0.90}Ni_{0.10}CoGe$ as also observed in magnetic measurements (~ 265 K; Fig. 2(e)). Differences in transition temperatures are probably associated with differences between the rates at which the magnetic and DSC measurements were carried out.

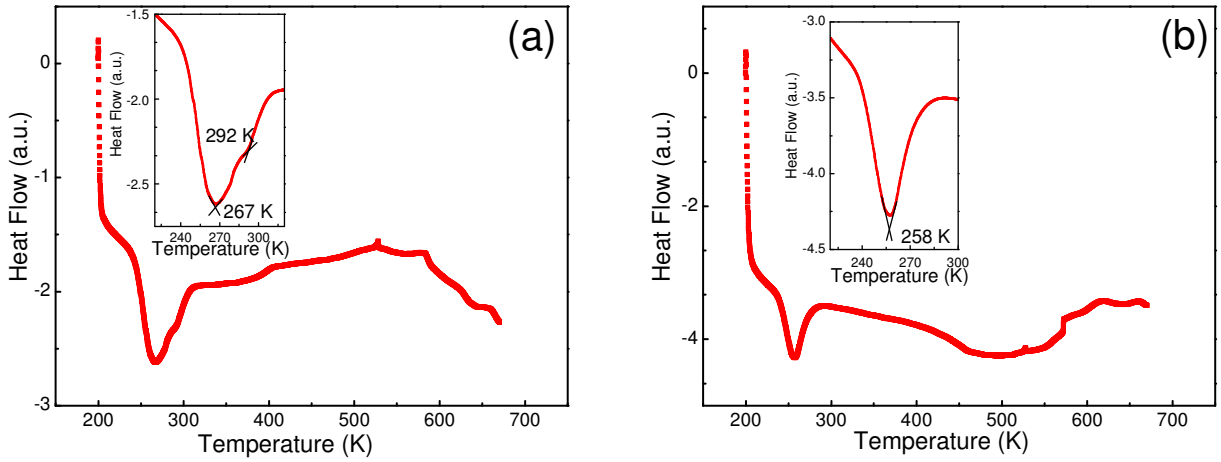

Fig. 3 DSC curves for (a) $Mn_{0.92}Ge_{0.08}CoGe$ and (b) $Mn_{0.90}Ni_{0.10}CoGe$ with insets showing the preliminary analyses of the transition temperatures.

4. Conclusions

The effects of substituting Fe and Ni atoms for Mn on the structural and magnetic transitions in $Mn_{1-x}Fe_xCoGe$ and $Mn_{1-x}Ni_xCoGe$ (x = 0.04 - 1.0) have been investigated over the temperature range 5 - 350 K by x-ray diffraction, magnetisation and DSC measurements. The impurity phase $MnCo_2Ge$ was obtained in all samples. The isothermal entropy changes for $Mn_{0.92}Fe_{0.08}CoGe$ are -ΔS ~ 5.6 J/kg·K at ~ 262 K and ~ 5.0 J/kg·K at ~ 283 K and for $Mn_{0.90}Ni_{0.10}CoGe$ -ΔS ~ 8.0 J/kg·K at ~ 258 K (ΔB = 0 - 5 T). Investigations are continuing to obtain samples free of $MnCo_2Ge$ and to obtain combined magnetic and structural entropy changes around a common transition temperature to maximise the magnetocaloric effects.

Acknowledgments

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