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The magneto-structural transition in Mn_{1-x}Fe_xCoGe

Abstract

Large refrigeration capacities, between 212(30) J kg⁻¹ and 261(40) J kg⁻¹ for a magnetic field change from 0 T to 5 T, were obtained in Mn_{1-x}Fe_xCoGe ($x = 0.01, 0.02, 0.03$ and 0.04) compounds. A partial magnetic phase diagram has been derived on the basis of magnetic transition and martensitic transformation temperatures determined from differential scanning calorimetry (200 K to 450 K), variable temperature x-ray diffraction (20 K to 310 K) and magnetisation measurements (5 K to 340 K; 0.01 T). Mn_{1-x}Fe_xCoGe compounds with compositions in the range $x = 0.01$ to 0.03 exhibit magneto-structural transitions. Neutron diffraction experiments were carried out on the Mn_{0.98}Fe_{0.02}CoGe sample over the temperature range of 5 K to 450 K. The diffraction patterns were analysed based on irreducible representation theory which confirms a ferromagnetic structure in the sample with an atomic magnetic moment of 3.7(1) μ B at 5 K on the Mn sublattice, oriented along the orthorhombic c axis. More significantly, a magneto-structural transition around $T_M \sim 297(1)$ K with a full width at half maximum of 29 K is demonstrated directly via neutron diffraction. Larger magnetic entropy changes are obtained for the Mn_{1-x}Fe_xCoGe ($x = 0.01, 0.02$ and 0.03) samples than for Mn_{0.96}Fe_{0.04}CoGe which has separate structural and magnetic transitions. In addition, it is noted that standard Arrott plots do not provide unambiguous insight to the nature of the magneto-structural transition in the Mn_{1-x}Fe_xCoGe compounds.

Keywords

magneto, structural, transition, mn1, xfexcoge

Disciplines

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The magneto-structural transition in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$

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Abstract:

Large refrigeration capacities, between $212(30) \text{ J kg}^{-1}$ and $261(40) \text{ J kg}^{-1}$ for a magnetic field change from 0 T to 5 T, were obtained in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02, 0.03$ and 0.04) compounds. A partial magnetic phase diagram has been derived on the basis of magnetic transition and martensitic transformation temperatures determined from differential scanning calorimetry (200 K to 450 K), variable temperature x-ray diffraction (20 K to 310 K) and magnetisation measurements (5 K to 340 K; 0.01 T). $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ compounds with compositions in the range $x = 0.01$ to 0.03 exhibit magneto-structural transitions. Neutron diffraction experiments were carried out on the $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ sample over the temperature range of 5 K to 450 K. The diffraction patterns were analysed based on irreducible representation theory which confirms a ferromagnetic structure in the sample with an atomic magnetic moment of $3.7(1) \mu_B$ at 5 K on the Mn sublattice, oriented along the orthorhombic c axis. More significantly, a magneto-structural transition around $T_M \sim 297(1) \text{ K}$ with a full width at half maximum of 29 K is demonstrated directly via neutron diffraction. Larger magnetic entropy changes are obtained for the $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02$ and 0.03) samples than for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ which has separate structural and magnetic transitions. In addition, it is noted that standard Arrott plots do not provide unambiguous insight to the nature of the magneto-structural transition in the $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ compounds.

I. INTRODUCTION

Among energy-saving and environmentally friendly technologies, magnetic refrigeration based on the magnetocaloric effect (MCE) has emerged as an alternative to conventional vapour-cycle refrigeration. The latter involve ozone depleting or hazardous chemicals and greenhouse gases [1, 2]. Vapour-cycle refrigeration also shows significantly lower cooling efficiencies than magnetic refrigeration [1, 2]. After the original discovery of MCE in Ni by Weiss and Piccard [3, 4], magnetic cooling technology was applied to obtain ultralow temperatures (< 1 K) [5, 6]. The discovery of a so-called giant MCE in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ close to room temperature, through the coincidence of magnetic and structural transitions (first order magneto-structural transition), re-ignited aspirations of extending this technique to more widespread practical use [7]. Recently, more than eight groups of compounds have been studied and proposed as well performing MCE materials [7-14], e.g. Heusler-type Ni-Mn-Ga alloys [9] and $\text{MnFe}(\text{P,As})$ [11]. As with $\text{Gd}_5\text{Si}_2\text{Ge}_2$, these materials also show magnetic-structural transitions. This strong coupling between the crystallography and magnetism leads to a simultaneous change of magnetic and lattice entropies when a magnetic field is applied, and thereby a large MCE.

MnCoGe-based compounds are a group of alloys in which a magneto-structural transition and consequently a large MCE [15-17] are readily achieved around room temperature, at a lower price compared with materials containing rare earth elements [14, 18]. Two stable phases exist in this series of compounds. For pure MnCoGe, a TiNiSi-type orthorhombic structure (Pnma) is formed from the Ni_2In -type hexagonal structure ($\text{P6}_3/\text{mmc}$) through a martensitic transformation at T_M , determined as ~ 398 K to ~ 458 K by Johnson [19] or ~ 650 K by Kanomata *et al.* [20], with a Curie temperature $T_C^{\text{orth}} \sim 345$ K [21]. Importantly, the martensitic transformation temperature T_M can be tuned easily [12, 22-24]. Slight compositional changes, achieved via doping for example [25, 26], can stabilise the hexagonal

phase to low temperature with a ferromagnetic transition occurring in the hexagonal phase at the Curie temperature $T_C^{\text{hex}} \sim 275$ K [27]. Therefore, if T_M is lowered to within the temperature range between T_C^{orth} and T_C^{hex} , a magneto-structural transition can occur, with potential for an enhanced MCE.

Fe is a suitable and effective substitute for Mn to decrease the martensitic transformation temperature T_M , as indicated by several papers [28-33]. Li *et al.* [29] presented a magneto-structural transition and large MCE in $\text{Mn}_{0.97}\text{Fe}_{0.03}\text{CoGe}$ ($-\Delta S_M = 10.6$ J kg⁻¹ K⁻¹ for a field change from 0 T to 5 T). *In situ* synchrotron high-energy x-ray diffraction experiments demonstrated the magnetic field-induced martensitic transformation in $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{CoGe}$ [30]. In our earlier work, we reported a large MCE of 10 J kg⁻¹ K⁻¹ (for a field change from 0 T to 5 T) for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ and also reported preliminary irreducible-representational analysis of neutron diffraction patterns collected at 20 K and 365 K [31]. In the present work, our study is expanded to include the influence of the martensitic transformation on the magnetocaloric effect in MnCoGe doped with Fe on the Mn crystallographic site. $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with $x \leq 0.04$ alloys in the as-prepared state are examined in detail. Different phase transitions in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02, 0.03$ and 0.04) compounds are revealed and the nature of these phase transitions discussed.

II. EXPERIMENTAL DETAILS

Polycrystalline $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ samples with $x = 0.01, 0.02, 0.03$ and 0.04 were prepared by arc melting stoichiometric amounts of Fe, Co, Ge and Mn (purities > 99.95 wt%) under an argon atmosphere on a water cooled Cu hearth. The ingots were melted four times to ensure homogeneity; 3% excess Mn was added to compensate for mass loss during the melting process. The powder x-ray diffraction patterns of all samples can be indexed to the Ni_2In -type

hexagonal structure or/and the TiNiSi-type orthorhombic structure with no evidence of any impurity phases. Samples were studied in the as-prepared state.

The differential scanning calorimetry (DSC) measurements were carried out from 200 K to 450 K at a ramp rate of 10 K/min on warming and cooling, leading to the determination of phase transition temperatures. Phase evolutions with increasing temperature were studied by x-ray diffraction over the temperature range between 20 K and 310 K using a PANalytical diffractometer with $\text{CuK}\alpha$ radiation. The temperature step was 50 K below the transition temperatures and 5 K within the martensitic transformation temperature range. A hold time of 20 min was used at every temperature step to ensure thermal equilibrium. Neutron powder diffraction experiments were performed for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ over the temperature range 5 K to 450 K upon warming in zero magnetic field on the high-intensity powder diffractometer Wombat ($\lambda = 2.4205 \text{ \AA}$) at the OPAL reactor, Australia. Refinements of both the x-ray diffraction and neutron patterns were performed using the Rietveld method using the program FullProf [34, 35].

Magnetisation measurements were carried out on a Quantum Design physical property measurement system (PPMS). The magnetisation versus temperature at constant-field sweeps were performed in an applied magnetic field of 0.01 T with 10 K steps over the temperature range from 5 K to 175 K and 5 K steps between 180 K and 340 K. Two measurement sequences were used: heating after zero-field cooling (ZFC) and field cooling (FC). For ZFC, the sample was cooled to 5 K in zero applied field and then the ZFC data were collected on warming in the applied magnetic field. The FC data were obtained during cooling from 340 K to base temperature $\sim 5 \text{ K}$ in the field of 0.01 T. The field dependence of the isothermal magnetisation was recorded in magnetic fields up to 8 T in steps of 0.2 T, from 205 K to 320 K in steps of 5 K.

III. RESULTS AND DISCUSSION

A. Crystallographic structural transitions

The differential scanning calorimetry results for all the compounds are shown in Fig. 1 with large exothermic and endothermic peaks evident in the cooling and warming curves respectively. The peak positions of the differential scanning calorimetry curves were used to determine the phase transition temperatures, denoted by $T_{\text{DSC}}^{\text{C}}$ and $T_{\text{DSC}}^{\text{W}}$ for cooling and warming curves respectively. The resultant phase transition temperatures are summarised in Table 1.

The x-ray diffraction patterns for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with $x = 0.01, 0.02, 0.03$ and 0.04 collected at 300 K and 200 K are shown in Fig. 2a and Fig. 2b, respectively. Refinement of the x-ray diffraction pattern of $\text{Mn}_{0.99}\text{Fe}_{0.01}\text{CoGe}$ indicates that the hexagonal and the orthorhombic structures coexist at 300 K, amounting to 29(1) wt% for the hexagonal structure and 71(1) wt% for the orthorhombic structure. The orthorhombic structure is transformed gradually to the hexagonal structure with increasing Fe concentration; and the hexagonal structure dominates in the $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ sample at 300 K (> 97(1) wt%). However, lower temperatures favour the stabilisation of the orthorhombic structure, e.g. the orthorhombic structure dominates in all of the four $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ samples at 200 K (> 90 wt%) as shown in Fig. 2b.

The evolutions of the orthorhombic phase and the hexagonal phase for all $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ samples ($x = 0.01, 0.02, 0.03$ and 0.04) were investigated by variable temperature x-ray diffraction upon warming from 20 K to 310 K. The fractions of the hexagonal and orthorhombic phases and their corresponding lattice parameters were obtained from Rietveld refinements of the x-ray diffraction patterns. As an example, in Fig. 2c we show the Rietveld refinement of the x-ray diffraction pattern of $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ collected at 250 K. The reliability factors for this Rietveld refinement are $R_p = 6.80$, $R_{wp} = 8.72$, $R_{exp} = 6.74$, and $\chi^2 = 1.67$. A Gaussian function was employed to analyse the martensitic transformation

distribution from the orthorhombic phase to the hexagonal phase, which was described in detail by Liu *et al.* in Ref. [36]. As an example, the martensitic transition temperatures T_M for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ was determined as 248(1) K with a full width at half maximum of 46(3) K, as shown in the inset of Fig. 2c. Corresponding results for all the four samples are summarised in Table 1.

The relationship between the lattice constants and martensitic transformation temperatures of the $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ samples with $x = 0.01, 0.02, 0.03$ and 0.04 is illustrated in Fig. 2d. The dash-dot line with square symbols in Fig. 2d indicates the decrease of the orthorhombic phase cell volume in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with increasing Fe concentration at 200 K (this temperature was chosen to be well clear of the phase transition where an accurate comparison of lattice constants is difficult); this decrease is accompanied by an obvious lowering of the transition temperatures T_M . Valence-electron localisation function (ELF) calculations demonstrate that a smaller Mn-Mn distance would lead to an enhancement of the covalent bonding between neighbouring Mn and Mn atoms in the hexagonal phase, thereby stabilising the hexagonal phase [37, 38]. Here, the substitution of Fe for Mn (covalent radii: $r_{\text{Fe}} = 1.25 \text{ \AA}$, $r_{\text{Mn}} = 1.39 \text{ \AA}$) leads to a decrease in the average lattice parameters and drives T_M towards lower temperatures.

B. Neutron experiments and magnetic structures

Neutron diffraction patterns for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ from 200 K to 380 K are presented in Fig. 3a. From these data, it is seen that the orthorhombic structure dominates at low temperature (below $\sim 265 \text{ K}$) with the hexagonal structure evident at high temperature (above $\sim 315 \text{ K}$). This is reflected by the phase fractions shown as a function of temperature in Fig 4b and, as discussed below, is in good agreement with the x-ray diffraction results reported previously [31]. The martensitic transformation from the orthorhombic phase to the hexagonal phase

occurs between 265 K and 315 K where both structures coexist. This is also in good agreement with the variable temperature x-ray diffraction result reported previously [31].

The neutron diffraction patterns were refined using the FullProf software [34, 35]. The data were fitted using the model described previously [31] although a “6-coefficient polynomial function” was used to fit the background rather than the “linear interpolation” used before. Several small peaks considered previously [31] as due to CoO impurity in fact are identified as a background contribution stemming from the sample cryostat. Only the Mn sublattice in the orthorhombic phase carries a significant magnetic moment. Below the Curie temperature of the hexagonal phase $T_C^{\text{hex}} \sim 275$ K [27], less than 10 wt% of the $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ sample adopts the hexagonal structure with this fraction decreasing to less than 4 wt% below 250 K (see Fig. 4b). Thus, the magnetic contribution from this small fraction of the hexagonal phase was ignored in the refinements. The resulting Rietveld refinement of the neutron diffraction pattern for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ collected at 295 K is shown in Fig. 3b. The reliability factors for this Rietveld refinement result are $R_p = 1.75$, $R_{wp} = 2.21$, $R_{exp} = 1.61$, and $\chi^2 = 1.89$.

The changes in lattice constants and cell volumes for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ near the martensitic transformation are plotted in Fig. 4a. The relationship of the lattice parameters and volumes between the two structures were determined as: $a_{\text{orth}} \sim c_{\text{hex}}$, $b_{\text{orth}} \sim a_{\text{hex}}$, $c_{\text{orth}}/\sqrt{3} \sim a_{\text{hex}}$ and $V_{\text{orth}}/2 \sim V_{\text{hex}}$ [19, 37]. The detailed evolutions of the orthorhombic and hexagonal phase from 5 K to 450 K are illustrated in Fig. 4b. Once again, a Gaussian model was used to fit the phase fraction evolutions [31], and the martensitic transformation temperature was determined as $\sim 296(1)$ K (denoted as T_M^{ND}) with a full width at half maximum of 29 K, accompanied by a cell volume reduction of $\Delta V/V = 4.1\%$, in good agreement with the results ($T_M \sim 297(1)$ K) from temperature-variable x-ray diffraction experiments.

The magnetic moment on the Mn sublattice in the orthorhombic phase (μ_{Mn}), derived from the Rietveld refinement of the neutron diffraction patterns as a function of temperature is shown in Fig. 4c. At 5 K, $\mu_{\text{Mn}} = 3.7(1) \mu_{\text{B}}$ which matches the value of $\mu_{\text{Mn}} = 3.67(1) \mu_{\text{B}}$ obtained from the saturation magnetisation at 5 K [31]. This moment value is also in accord with the value of $3.6 \mu_{\text{B}}$ for $(\text{MnCo})_{0.97}\text{Ge}$ at 4.2 K reported by Markin and Mushnikov [39]. The solid line in Fig. 4c shows a fit to the temperature variation of the magnetic moment on the Mn sublattice of the orthorhombic phase using a Brillouin function with an angular momentum quantum number of Mn^{2+} , $J = S = 5/2$. As shown in Fig. 4c, extrapolation of the fit to the Brillouin function leads to a Curie temperature for the orthorhombic phase of the $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ sample of $T_{\text{C}}^{\text{orth}} = 397(6) \text{ K}$. This value is significantly larger than the 345 K reported for annealed pure MnCoGe by Song *et al.* [21]. One possible reason that may account in part for this difference may be the chemical pressure introduced by the substitution of Fe for Mn. Work by Kanomata, *et al.* [20] demonstrated that applied pressure can drive the Curie temperature ($T_{\text{C}}^{\text{orth}}$) for the orthorhombic MnCoGe phase towards higher temperatures ($dT_{\text{C}}/dp = 39 \text{ K/GPa}$). Here we use the Murnaghan equation to describe the lattice response to pressure [40]:

$$P(V) = \frac{B_0}{B'_0} \left(\left(\frac{V_0}{V} \right)^{B'_0} - 1 \right). \quad (1)$$

P is the pressure correlated to the change of volume (V), and B'_0 is defined as:

$$B' = B_0 + B'_0 P \quad (2)$$

where B' is used to describe the pressure dependence of the bulk modulus, and B_0 is the bulk modulus at ambient pressure. Based on the results for $\text{Mn}_{0.92}\text{Fe}_{0.08}\text{CoGe}$ [32] for which bulk modulus $B_0 \sim 112.2 \text{ GPa}$ and the first derivative with respect to pressure $B'_0 \sim 7.2$, the chemical pressure for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ was determined as 0.396 GPa. This in turn indicates that the increase of Curie temperature from chemical pressure is $\sim 15.4 \text{ K}$. This value is only

an approximation although is nevertheless smaller than the difference between our value of $T_C^{\text{orth}} = 397(6)$ K and the previously reported value of 345 K for MnCoGe [21]. In addition, vacancies introduced in the sample preparation (as-prepared state) may also play a role in influencing the chemical pressure and therefore the magnetic transition.

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C. Magnetisation and partial magnetic phase diagram

Normalised magnetisation curves of the four samples are shown in Fig. 5a. The magnetic phase transition temperatures were determined from the temperature derivative of the magnetisation, dM/dT , (*e.g.* [40]). Two examples of the differential magnetisation curves for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ and $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ are shown in Fig. 5b.

In the case of $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$, the magnetisation curves for ZFC and FC show changes at $\sim 300(4)$ K and $\sim 290(4)$ K, respectively (Fig. 5a and Fig. 5b). These two temperature points straddle the martensitic transformation temperature T_M determined previously from the variable temperature x-ray diffraction patterns [31], $\sim 290(4)$ K $< T_M$ ($\sim 297(1)$ K) $< \sim 300(4)$ K, indicating the coupling of the structural and magnetic transitions. These results are in agreement with the analyses of the neutron diffraction patterns of Fig. 3, which are presented in the graphs of phase fractions and magnetic moment versus temperature shown in Fig. 4b and Fig. 4c and indicate the magneto-structural nature of the transition at $T_M \sim 297$ K from ferromagnetic-orthorhombic to paramagnetic-hexagonal.

Similar results were obtained for $\text{Mn}_{0.99}\text{Fe}_{0.01}\text{CoGe}$ and $\text{Mn}_{0.97}\text{Fe}_{0.03}\text{CoGe}$, demonstrating that magneto-structural transitions are also formed in these two samples. The magneto-structural transition temperatures for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with $x = 0.01, 0.02$ and 0.03 are the martensitic transformation temperature T_M determined by variable temperature x-ray diffraction as

discussed in section B and listed in Table 1: namely, 316 K, 297 K and 277 K, respectively. Another point to note is that the changes in the magnetisation curves of $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02$ and 0.03) are due to the magneto-structural transition from the ferromagnetic orthorhombic structure to the paramagnetic hexagonal structure, rather than a pure magnetic phase transition at the corresponding Curie temperatures. To clearly indicate these differences (from general magnetic ordering at a corresponding Curie temperature), the transition temperatures here are denoted as T_m^W and T_m^C for the ZFC and FC magnetisation curves, respectively as listed in Table 1.

For the $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ sample, two changes are observed in the magnetisation curve (Fig. 5a) - a pronounced change in magnetisation around 275(3) K and a further change in magnetisation around 248 K. No obvious thermal hysteresis is observed around 275(3) K which is deemed to be a magnetic phase transition at the Curie temperature ($T_C^{\text{hex}} \sim 275(3)$ K), of the sample's hexagonal phase. Another magnetisation change around 248(1) K presents thermal hysteresis. This temperature matches with the martensitic transformation temperature T_M determined from variable temperature x-ray diffraction as shown in Fig. 2c. Given the nonzero magnetisation below and above T_M , this transition is considered as a transition from the ferromagnetic orthorhombic phase to the ferromagnetic hexagonal phase. The magnetic properties for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ are similar to those obtained for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ as demonstrated by neutron experiments [25]. In the case of $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$, the transition temperatures were $T_C^{\text{hex}} \sim 270$ K and $T_M \sim 235$ K. In both samples, substitution for Mn drives the martensitic transformation temperature T_M below the Curie temperature of the hexagonal structure T_C^{hex} .

Using the phase transition temperatures derived from differential scanning calorimetry (200 K to 450 K), x-ray diffraction (20 K to 310 K) and magnetisation (5 K to 340 K), a partial magnetic phase diagram can be constructed as shown in Fig. 6. This diagram shows some

similarities to, but also some differences from the results for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ compounds reported by Li *et al.* [29] and for $\text{Mn}_{1-x}\text{Ni}_x\text{CoGe}$ compounds reported by Zhang *et al.* [41]. The magneto-structural transition occurs in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ when $x \leq 0.5$ [29] and in $\text{Mn}_{1-x}\text{Ni}_x\text{CoGe}$ when $0.07 \leq x \leq 0.12$. All of these values are different from our samples $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with $x = 0.01, 0.02$ and 0.03 . These differences are likely to be due to the different heat treatment histories: the present samples are in the as-prepared state, while the $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ and $\text{Mn}_{1-x}\text{Ni}_x\text{CoGe}$ compounds reported previously were annealed. Vacancies resulting from the sample preparation will remain in the as-prepared MnCoGe alloys and these vacancies are likely to drive the martensitic transformation temperature T_M towards lower temperature [24, 42]. In other words, a smaller Fe concentration in the as-prepared $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ can produce the same T_M as found in the annealed $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with a higher Fe concentration.

This partial phase diagram (Fig. 6) is helpful for exploring the magnetocaloric effect. The arrow marked as I is the typical cooling route for samples, e.g. $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with $x = 0.02$, which exhibits a single magneto-structural transition. As discussed below in Section D, this behaviour for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ implies that the $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ sample will exhibit a large magnetocaloric effect. By comparison the route at arrow II is at a point with two separated phase transitions where the martensitic transformation temperature for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ is below the Curie temperature of the hexagonal structure T_C^{hex} . $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ undergoes a magnetic phase transition at the Curie temperature $T_C^{\text{hex}} \sim 275(3)$ K and then a martensitic transition from the ferromagnetic hexagonal phase to the ferromagnetic orthorhombic phase at $T_M \sim 248(1)$ K. Thus, we expect two peaks in the magnetic entropy change for the $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ sample.

D. Magnetocaloric effect and refrigerant capacity

The isothermal magnetic entropy changes were calculated using the standard Maxwell function for magnetic field changes over the ranges 0 T to 2 T and 0 T to 5 T:

$$\Delta S_M = \int_0^B \left(\frac{\partial M(T, B')}{\partial T} \right) dB' \quad (1)$$

The changes in magnetic entropy of the four $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ samples ($x = 0.01, 0.02, 0.03, 0.04$) with magnetic field changes of $\Delta B = 0 \text{ T to } 2 \text{ T}$ and $\Delta B = 0 \text{ T to } 5 \text{ T}$ are shown in Fig. 7a with the entropy values listed in Table 2. As expected, temperature points corresponding to the entropy change peaks decrease with increasing doping concentration. Given that magneto-structural transitions occur in the $\text{Mn}_{0.99}\text{Fe}_{0.01}\text{CoGe}$, $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ and $\text{Mn}_{0.97}\text{Fe}_{0.03}\text{CoGe}$ samples, as expected the $-\Delta S_M$ values for these three samples are larger than the $-\Delta S_M$ value of the $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ sample (Fig. 7a) for which two separate transitions are obtained as indicated from route II of Fig. 6. The positions of the peaks in the entropy change were determined with a magnetic field change of 0 T to 2 T. As shown in Fig. 7b, the entropy changes for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ and $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ ($\Delta B = 0 \text{ T to } 2 \text{ T}$), were fitted using the Voigt lineshape (fitting with Gaussian and Lorentzian curves were also applied but the best fits were obtained with the Voigt function). The single peak for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ is centred at 295(1) K, leading to the entropy value $-\Delta S_M^{\text{peak}} = 4.0(6) \text{ J kg}^{-1} \text{ K}^{-1}$. The two peaks in entropy for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ are located at $T_M = 247(1) \text{ K}$ and $T_C^{\text{hex}} = 275(1) \text{ K}$ with $-\Delta S_M^{\text{peak}} = 1.9(4) \text{ J kg}^{-1} \text{ K}^{-1}$ and $-\Delta S_M^{\text{peak}} = 1.3(3) \text{ J kg}^{-1} \text{ K}^{-1}$ respectively. The transitions at T_M and T_C^{hex} are consistent with the two transitions of $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ indicated by arrow II in the partial phase diagram (Fig. 6).

Standard Arrott plots [43] are often used to investigate the nature of magnetic transitions. The occurrence of a positive slope in the Arrott plots around a magnetic phase transition signals the second-order nature of this transition, whereas a negative slope implies a first-order nature [40, 43, 44]. The Arrott plots of M^2 versus B/M for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ are shown in Fig.

8 around the martensitic transition $T_M \sim 297$ K, and reveal positive slopes. Following the Arrott-plots criterion, the magneto-structural transition in $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ would be classified as second-order. However, this contradicts the observed physical phenomena: the change of structure connected directly to the change of magnetization (as shown in section C) and the thermal hysteresis as shown in, for example, Table 1 and Fig. 6. Difficulties in determining the nature of the phase transitions in some samples using Arrott plots have been reported recently [45]. For example, $\text{Mn}_{1.3}\text{Fe}_{0.7}\text{P}_{0.6}\text{Si}_{0.25}\text{Ge}_{0.15}$ undergoes a first-order phase transition at ~ 250 K, but shows some characteristics of a second-order phase transition in its Arrott plots [45]. It is clear that standard Arrott plots alone do not provide unambiguous insight to the order of a magneto-structural transition in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ compounds.

The refrigerant capacity (RC), which is defined as $\text{RC} = \int_{T_{r1}}^{T_{r2}} |\Delta S_M| dT$, is a useful parameter in evaluating the potential of a MCE material. It is a measure of how much heat can be transferred between the cold and hot sinks during one ideal refrigeration cycle [46, 47]. RC values for the four samples were calculated based on the curves fitted to the entropy changes. RC values between $212(30) \text{ J kg}^{-1}$ and $261(40) \text{ J kg}^{-1}$ for a magnetic field change from 0 T to 5 T were obtained for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02, 0.03$ and 0.04), as shown in Table 2. These RC values are larger than the values of 184 J kg^{-1} obtained for $\text{MnCoGe}_{0.95}\text{Ga}_{0.05}$ [48] or 159 J kg^{-1} for $\text{Mn}_{0.9}\text{Ni}_{0.1}\text{CoGe}$ [49], and comparable with 240 J kg^{-1} for $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{CoGe}$ [33] (with a field change of 5 T).

IV. Conclusions

A partial magnetic phase diagram has been established for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02, 0.03$ and 0.04) alloys in the as-prepared state after comprehensive investigations using differential scanning calorimetry (200 K to 450 K), x-ray diffraction (20 K to 310 K) and magnetisation (5 K to 340 K) measurements. Increasing Fe doping reduces the martensitic

transformation temperature T_M from 316(1) K for $\text{Mn}_{0.99}\text{Fe}_{0.01}\text{CoGe}$ to 240(1) K for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$. This leads to the formation of magneto-structural transitions in $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02$ and 0.03) compounds, and confirmed using neutron diffraction (5 K to 450 K). However two separate transitions occur in $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ - a structural transition at 248(1) K and a magnetic transition at 275(1) K. The analysis of the $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ neutron diffraction patterns revealed a ferromagnetic structure in the sample with a magnetic moment of 3.7(1) μ_B at 5 K on the Mn sublattice, oriented along the c axis in the orthorhombic phase. The largest magnetic entropy change was obtained at the single magneto-structural transition $T_M = 297(1)$ K in $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ as $-\Delta S_M^{\text{peak}} \sim 4.0(6)$ J kg^{-1} K^{-1} ($\Delta B = 0$ T to 2 T), while two MCE peaks were obtained for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ with $-\Delta S_M^{\text{peak}} \sim 1.9(4)$ and $1.3(3)$ J kg^{-1} K^{-1} for a field change of $\Delta B = 0$ T to 2 T at the martensitic transition temperature $T_M \sim 248(1)$ K and magnetic transition temperature $T_C^{\text{hex}} \sim 275(1)$ K, respectively.

Analysis of the magneto-structural transition in $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ using conventional Arrott plots was inconclusive regarding the nature of this transition. Finally, a large refrigeration capacity ($\text{RC} = 212(30)$ J kg^{-1} to $\text{RC} = 261(40)$ J kg^{-1} for a magnetic field change of 5 T) means $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ is promising candidate for the exploration of magnetic refrigeration technology. Attaining such RC values in the as-prepared state of potential magnetic refrigeration materials is an advantage as costs associated with furnace annealing treatments are not necessary.

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Figures:

Fig. 1 (colour online) Normalised differential scanning calorimetry curves for Mn_{1-x}Fe_xCoGe ($x = 0.01, 0.02, 0.03$ and 0.04) with a ramp rate of 10 K/min. Phase transition temperatures are determined according to the peak positions: *e.g.* $T_{\text{DSC}}^{\text{w}} \sim 315$ K and $T_{\text{DSC}}^{\text{c}} \sim 300$ K for Mn_{0.99}Fe_{0.01}CoGe based on warming and cooling curves respectively.

Fig. 2 (colour online) (a) X-ray diffraction patterns for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02, 0.03$ and 0.04) collected at 300 K. The Miller indices for the hexagonal and orthorhombic structures are designated with and without an asterisk *, respectively. (b) X-ray diffraction patterns for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ ($x = 0.01, 0.02, 0.03$ and 0.04) collected at 200 K. (c) Rietveld refinement of the x-ray diffraction pattern for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ collected at 250 K. The horizontal rows of Bragg markers (top to bottom) represent the hexagonal and orthorhombic structures, respectively. The inset shows the temperature dependence of the phase fractions (wt%) for the hexagonal and orthorhombic structures in $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ between 200 K and 310 K. (d) Cell volume variation of the orthorhombic phase of $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ versus Fe concentration at 200 K and the martensitic transformation temperatures T_M determined from variable temperature x-ray diffraction experiments as described in the text.

Fig. 3 (colour online) (a) Neutron diffraction patterns for as-prepared $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ over the temperature range of 205–380 K at 5 K intervals. Above 315 K, the sample predominately exhibits the hexagonal structure (orange colour and Miller indices with asterisk); and the orthorhombic structure dominates below 265 K (olive colour and Miller indices without asterisk). A structural transition occurs in the range 265–315 K where both structures coexist (blue colour). (b) Rietveld refinement of the neutron diffraction pattern for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ collected at 295 K. The horizontal rows of Bragg markers (top to bottom) represent the nuclear structure of the orthorhombic phase, the magnetic structure of the orthorhombic phase and the nuclear structure of the hexagonal phase, respectively.

I FIND THE DISCUSSION OF COLOURS IN FIGURES 2 AND 3 CONFUSING. GREEN RARELY DISPLAYS CLEARLY AND SUGGEST WE CHANGE ALL GREENS. MUST HAVE CONSISTENCY BETWEEN FIGURES 2 AND 3; WE SEEM TO HAVE GREEN PATTERNS AND GREEN LABELS FOR A DIFFERENT PHASE, NEED TO STANDARDISE. ALSO OLIVE IS NOT COMMONLY USED AS A DESCRIPTOR OF COLOUR. TRY TO OBTAIN A CLEAR TREND, FOR EXAMPLE BLUE IS USED TO DENOTE THE ORTHORHOMBIC PHASE IN FIGURE 2C, WHY NOT USE BLUE FOR THE ORTHORHOMBIC PATTERNS? SUGGEST WE USE THE SAME COLOURS THROUGHOUT TO DENOTE THE SAME PHASES; AGAIN IN FIGURE 4 WE HAVE A VARIETY OF COLOURS TO DENOTE THE SAME PHASES – THAT DOES NOT MAKE SENSE. OVERALL THE SELECTIONS OF COLOURS SEEM TO CREATE UNNECESSARY ISSUES.

Fig. 5 (colour online) (a) Normalised magnetisation curves as a function of temperature for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ in an applied field of 0.01 T on heating after zero-field cooling (ZFC, solid lines) and field cooling (FC, dash lines). (b) The differential dM/dT curves versus T for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ and $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$.

THE ARROWS ARE TOO CLOSE IN FIG 5A – THE WARMING ARROW SHOULD BE MOVED OUTSIDE THE FULL LINE

HOWEVER THESE ARROWS STILL SEEM INCORRECT – THE CAPTION FOR FIG 5A SAYS HEATING – SO HOW COME ARROWS INDICATE COOLING AND WARMING?? THIS SEEMS TO BE CONFUSED WITH ZFC AND FC – NEED TO CHECK THESE POINTS.

Fig. 6 (colour online) Partial phase diagram of $Mn_{1-x}Fe_xCoGe$ ($x = 0 - 0.04$) determined from: variable temperature x-ray diffraction (solid line); differential scanning calorimetry (dashed lines); magnetisation curves (dot lines), and neutron diffraction experiments (asterisk). The solid symbols denote the results obtained on heating and the open symbols were obtained on cooling. The point marked by the red solid triangle in the warming differential scanning calorimetry curve is taken from the report by Johnson ([19], here ~ 398 K is selected). The arrow I is a typical route for samples with a magneto-structural transition. The arrow II shows a typical route with two separated phase transitions where the martensitic transformation temperature is tuned below the Curie temperature of the hexagonal structure T_C^{hex} .

Fig. 7 (colour online) (a) Isothermal magnetic entropy changes $-\Delta S_M$ as a function of temperature, calculated from the magnetisation isotherms for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ with increasing magnetic field changes ΔB of 2 T (dashed lines, starting from 0 T) and 5 T (solid lines). (b) Isothermal magnetic entropy changes $-\Delta S_M$ as a function of temperature for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$ (circles) and for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$ (triangles) with a magnetic field change of $\Delta B = 2$ T fitted using Voigt curves to determine the peak entropy changes: for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$, only one peak exists; for $\text{Mn}_{0.96}\text{Fe}_{0.04}\text{CoGe}$, peaks were found centred around ~ 247 K and ~ 274 K.

Fig 8. (colour online) Arrott plot of M^2 versus B/M at temperatures in the vicinity of T_M (~ 297 K) for $\text{Mn}_{0.98}\text{Fe}_{0.02}\text{CoGe}$.

Tables:

Table 1 Phase transition temperatures for $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ determined from differential scanning calorimetry, temperature-variable x-ray diffraction and magnetisation experiments.

x	$T_{\text{DSC}}^{\text{W}\dagger}$ (K)	$T_{\text{DSC}}^{\text{C}\dagger}$ (K)	$T_{\text{M}}^{\ddagger}$ (K)	FWHM ‡ (K)	$T_{\text{M}}^{\text{ND}\ddagger}$ (K)	T_{m}^{W} (K)	T_{m}^{C} (K)	T_{C} (K)
0.01	315(2)	300(2)	316(1)	54(3)	-	320(4)	310(4)	-§
0.02	296(2)	285(2)	297(1)	37(2)	296(1)	300(4)	290(4)	-
0.03	276(2)	267(2)	277(1)	42(3)	-	280(4)	275(4)	-
0.04	251(2)	240(2)	248(1)	46(3)	-	245(4)*	251(4)*	275(3)

† The superscripts W and C represent data collected upon warming and cooling, respectively.

‡ From variable temperature x-ray diffraction measurements upon warming. The phase evolutions were fitted using a Gaussian lineshape, and the peak centres were taken as the martensitic transformation temperatures T_{M} .

‡ From neutron diffraction measurements.

* Due partial overlap between the structural and magnetic transitions, it is difficult to determine the magnetic state change resulting from the phase transition from the ferromagnetic orthorhombic phase to the hexagonal phase. Therefore, T_{m}^{W} and T_{m}^{C} were determined by $T_{\text{M}} \pm$ thermal hysteresis.

§ Since a magneto-structural transition is present in the samples with $x = 0.01, 0.02$ and 0.03 , the magnetisation changes are marked as T_{M} rather than T_{C} .

AS IN MY COMMENTS THE RESPONSE, IS THIS INTERPRETATION OF THE REVIEWER'S COMMENT CORRECT? HE SEEMS TO BE SAYING T_{C} RATHER THAN T_{M} SHOULD BE USED?

Table 2 Information on the magnetic entropy changes of the $\text{Mn}_{1-x}\text{Fe}_x\text{CoGe}$ samples with a magnetic field change of 5 T.

x	$T_{\text{peak}}^{\dagger\dagger}$ (K)	$-\Delta S_{\text{M}}^{\text{peak}\dagger\dagger}$ (J kg ⁻¹ K ⁻¹)	FWHM †† (K)	$T_{\text{peak}}^{\ddagger\dagger}$ (K)	$-\Delta S_{\text{M}}^{\text{peak}\ddagger\dagger}$ (J kg ⁻¹ K ⁻¹)	FWHM ‡† (K)	RC $^{\boxtimes}$ (J kg ⁻¹)
0.01	310(4)	8(1)	36(5)	-	-	-	241(30)
0.02	295(4)	10(2)	27(5)	-	-	-	212(30)
0.03	276(4)	9(2)	31(5)	-	-	-	221(30)
0.04	247(4)	5(1)	28(5)	275(1)	2.6(5)	80(10)	261(40)

†† From a magneto-structural transition/martensitic transition.

‡‡ From a magnetic transition at the corresponding Curie temperature.

⊗ Refrigeration capacities calculated based on Voigt fitting lines of the entropy changes with a magnetic field change of 0 T to 5 T.