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Magnetocaloric effect and magnetostructural coupling in Mn$_{0.92}$Fe$_{0.08}$CoGe compound

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The structural properties of Mn$_{0.92}$Fe$_{0.08}$CoGe have been investigated in detail using synchrotron x-ray diffraction in zero and applied pressure (p = 0–10 GPa). A ferromagnetic transition occurs around T$_C$ = 300 K and a large magnetic-entropy change $-\Delta S_M = 17.3 \text{ J/kg K}$ detected at T$_C$ for a field change of AB = 5 T. The field dependence of $-\Delta S_M^{\text{max}}$ can be expressed as $-\Delta S_M^{\text{max}} \propto B$. At ambient temperature and pressure, Mn$_{0.92}$Fe$_{0.08}$CoGe exhibits a co-existence of the orthorhombic TiNiSi-type structure (space group Pnma) and hexagonal Ni$_3$In-type structure (space group P63/mmc). Application of external pressure drives a structure change from the orthorhombic TiNiSi-type structure to the hexagonal Ni$_3$In-type structure. A large anomaly in heat capacity around T$_C$ is detected and the Debye temperature $\theta_D (=319(\pm 10) \text{ K})$ has been derived from analyses of the low temperature heat capacity, T = 10 K. © 2015 AIP Publishing LLC.

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Magnetocaloric materials have attracted significant interests over the past two decades due to their possible applications as high efficiency, environmentally friendly heat pumps and refrigerators. This follows the discoveries reported by Pecharsky and Gschneider in 1997 related to magnetic entropy changes at ferromagnetic transitions in the Gd$_5$Si$_4$ series. More recently, compounds containing manganese such as MnFeP$_{0.45}$As$_{0.55}$, MnAs$_{1-x}$Sb$_x$, Ni-Mn-Sn-based alloys, Ni-Mn-Ga, RMn$_2$X$_3$-based, and MnCoGe/MnNiGe-based compounds have attracted significant attention due to their interesting magnetic properties and large entropy changes. These large entropy changes and related magneto-caloric effects result from the high sensitivity of Mn magnetic states to variations in the chemical environment.

Stoichiometric MnCoGe has an orthorhombic TiNiSi-type structure (space group Pnma) at low temperatures (below ~650 K) and exhibits a martensitic structural transformation from the low-temperature orthorhombic TiNiSi-type structure to a high-temperature hexagonal Ni$_3$In-type structure (space group P63/mmc) around T$_{\text{str}}$ = 650 K. The MnCoGe compounds in both structural states are ferromagnets but their magnetizations and Curie temperatures (T$_C$) differ considerably (T$_C$ = 345 K for the orthorhombic structure, T$_C$ = 275 K for the hexagonal structure). Importantly, the value of T$_{\text{str}}$ depends strongly on several factors including: external pressure, the vacancies in the Co and Mn sites, as well as variation in chemical environment due to element substitution on Mn, Co, or Ge sites. Recently, MnCoGe-based compounds have attracted significant attention; this is due mainly to the strong coupling between magnetism and structure in these materials. This coupling in turn can lead to MnCoGe-based materials, which exhibit large entropy changes and associated magnetocaloric effects, thereby offering scope for magnetic refrigeration around room temperature. In order to achieve coincidence of magnetic and structural transitions which differ by around 300 K in the parent MnCoGe compound, several approaches to modify the Mn environments have been adopted. Several studies concerning substitution of other elements for Mn, Co, or Ge have been reported in order to shift and thereby control the transition temperatures T$_{\text{str}}$ and T$_C$. The general aim of such studies is to cause the magnetic and structural transitions to coincide or overlap closely and thereby capitalise on both the magnetic and structural entropies at the resultant magnetostructural transition.

In this work, we report the structural and magnetic properties of Mn$_{0.92}$Fe$_{0.08}$CoGe compound as determined by high resolution, high intensity synchrotron x-ray diffraction studies and detailed magnetic measurements. We also report the influence of external pressure (0–10 GPa) on the structural properties of Mn$_{0.92}$Fe$_{0.08}$CoGe as determined by high resolution synchrotron studies.

Mn$_{0.92}$Fe$_{0.08}$CoGe was prepared by argon arc melting appropriate amounts of high purity elements on a water-cooled Cu hearth. Around 3% excess Mn was added to compensate for loss during melting. The sample was re-melted five times to ensure good homogeneity and annealed at 850 °C for 1
week in an evacuated quartz tube then quenched into water. X-ray diffraction (Cu K$_\alpha$) at room temperature confirmed that both the orthorhombic TiNiSi-type structure (space group Pnma) and hexagonal Ni$_2$In-type structure (space group P63/mmc) are present in the sample with no discernible impurity phases. The magnetic measurements were carried out using a Physical Property Measurement System over the temperature range of 5–300 K and at magnetic fields in the range of 0–8 T. The high pressure diffraction studies at room temperature were undertaken using the Powder Diffraction (PD) beamline at the Australian Synchrotron facility in the pressure range from ambient to 10 GPa using a diamond anvil cell.

Figure 1(a) shows a series of diffraction patterns for the Mn$_{0.92}$Fe$_{0.08}$CoGe compound collected at different pressures. At ambient pressure, it can be seen that there are mixtures of the orthorhombic TiNiSi-type structure (~61.4%) and the hexagonal Ni$_2$In-type structure (~38.6%). The lattice parameters for the orthorhombic structure have been derived to be $a = 5.910(6)$ Å, $b = 3.832(5)$ Å, $c = 7.083(6)$ Å, and $V = 160.4(3)$ Å$^3$, while $a = 4.089(4)$ Å, $c = 5.322(3)$ Å, and $V = 77.0(1)$ Å$^3$ for the hexagonal phase. On applying hydrostatic pressure above $p = 1.38$ GPa, the compound was found to exhibit only the hexagonal Ni$_2$In-type structure. This finding indicates that application of external pressure results in a phase transition from the orthorhombic TiNiSi-type structure of Mn$_{0.92}$Fe$_{0.08}$CoGe into the hexagonal Ni$_2$In-type structure. In other words, the external pressure is found to shift the structural transition temperature from above room temperature down to below room temperature. Rietveld refinements results of Mn$_{0.92}$Fe$_{0.08}$CoGe (FULLPROF software) at selected pressures are shown in Figure 1(b). Before applying pressure, there is around ~61% of the orthorhombic phase and ~39% of the hexagonal at room temperature. When the applied pressure is greater than $p \sim 1.38$ GPa, the structure of the entire sample changes to the hexagonal structure. However, it should be noted that on release of the pressure, the overall sample structures revert to a mixture of both orthorhombic and hexagonal of phase fractions ~78.6% orthorhombic and 21.4% hexagonal. This behaviour demonstrates that the structural modification by external pressure is partially reversible. The outcomes of our experiment indicate that external pressure drives the structure transition temperatures of Mn$_{0.92}$Fe$_{0.08}$CoGe down to below room temperature. This agrees well with the conclusion obtained for the parent MnCoGe compound by Niziol et al. who reported that external pressure can lead to a significant decrease in the transition temperature under hydrostatic pressure up to 1.3 GPa.

The pressure dependences of the lattice parameters derived from the refinements are shown in Figure 2. It can be seen from the variation of the $c/a$ ratio with pressure (inset to Figure 2(b)) that the contraction of the unit cell with pressure is anisotropic. It is well accepted that the lattice response to pressure can be described by the Murnaghan equation as

$$P(V) = \frac{B_0}{B_0'} \left( \frac{V_0}{V} \right)^{7/2} - 1 \quad (1)$$

or equivalently

$$V(P) = V_0 \left( 1 + \frac{B_0'}{B_0} P \right)^{-1/6} \quad (2)$$

where $V_0$, $B_0$, and $B_0'$ are the volume, bulk modulus, and its first derivative at ambient pressure, respectively.

The experimental data have been fitted with 3rd order of Murnaghan equation leading to the fitted results shown by the full line in Figure 2(b). The values of $B_0$ and $B_0'$ for Mn$_{0.92}$Fe$_{0.08}$CoGe have been derived to be 112.2 GPa and 7.2, respectively. By comparison, the values of $B_0$ for TbNi$_2$Mn and TbNi$_2$ (Ref. 18) are found to be 128 GPa and 103 GPa, respectively, while $B_0$ is only 68 GPa and 20 GPa for Pr$_{0.5}$Y$_{0.5}$Mn$_2$Ge$_2$ (Ref. 6) and TbMn$_2$, respectively.
The temperature dependence of the DC magnetization (see Figure 3) reveals only one magnetic phase transition in Mn$_{0.92}$Fe$_{0.08}$CoGe with $T_C = 300(\pm 5)$ K; this behaviour agrees well with the differential scanning calorimetry (DSC) measurements shown as the inset of Figure 3. This behaviour of a unique transition temperature in the magnetization and DSC results indicates that the structure and magnetic transitions coincide in this compound. The magnetization of Mn$_{0.92}$Fe$_{0.08}$CoGe as measured as a function of field over the temperature region 120 K to 350 K with 5 K steps is shown in Figure 4(a). The related Arrott plots of $M^2$ versus $B/M$ at selected temperatures are drawn in Figure 4(b) with the positive slopes of the Arrott plots around $T_C$ indicating that the magnetic transition around $T_C$ is second order. The isothermal entropy change $-\Delta S_M$ corresponding to magnetic field change $\Delta B$ (starting from zero field) can be conveniently derived from the magnetization data using the Maxwell relation [e.g., Refs. 2–6]

$$\Delta S_M(T, B) = \int_0^B \left( \frac{\partial M(T, B)}{\partial T} \right)_B dB.$$ 

The magnetocaloric entropy change determined in this way is shown in Figure 4(c) with the curves for decreasing field and increasing field found to be essentially identical. The maximum entropy changes for $\Delta B = 1$ T and $\Delta B = 5$ T are...
The temperature dependence of the heat capacity measurements $C_p(T)$ for Mn$_{0.92}$Fe$_{0.08}$CoGe at lower (2 K–120 K) and higher temperature (250 K–340 K) regions is shown in Figures 5(a) and 5(b), respectively. The pronounced anomaly observed around $T_C$ originates from coincidence of the structural and magnetic phase transitions. It is well accepted that the total heat capacity $C_p(T)$ includes three contributions from phonon $C_p^\text{ph}(T)$, electrons $C_p^\text{el}(T)$, and magnons $C_p^\text{m}(T)$, respectively. At low temperatures, the heat capacity can be described as $C(T) = \gamma T + \beta T^3$, where $\gamma$ and $\beta$ are the electronic contributions. From Figure 5(a), the values of $\gamma = 2.93$ mJ/mol K$^2$ and $\beta = 0.174$ mJ/mol K$^3$ have been derived. The Debye temperature $\theta_D$ can be obtained from the relation $\theta_D = 319(\pm 10)$ K, which is very close to the values reported for Mn$_{0.8}$Fe$_{0.2}$CoGe ($\theta_D = 306$ K) and CoMnGe$_{0.945}$Ga$_{0.055}$ ($\theta_D = 337$ K).

The structural and magnetic properties of Mn$_{0.92}$Fe$_{0.08}$CoGe have been investigated over the temperature range of 5–650 K. At ambient temperature and pressure, Mn$_{0.92}$Fe$_{0.08}$CoGe exhibits co-existence of the orthorhombic TiNiSi-type structure (space group Pnma) and hexagonal Ni$_3$In-type structure (space group P63/mmc). Application of external pressure (p = 1.38 GPa) drives a structure change from the orthorhombic TiNiSi-type structure to the hexagonal Ni$_3$In-type structure.

The Mn$_{0.92}$Fe$_{0.08}$CoGe compound exhibits a pronounced magnetostuctural transition around $T_C \approx 300$ K. A large magnetic-entropy change of $-\Delta S_M = 17.3$ J/kg K at $T_C$ for a field change of $\Delta B = 5$ T has been determined for the Mn$_{0.92}$Fe$_{0.08}$CoGe compound. The field dependence of $-\Delta S_M^\text{max}$ around $T_C$ can be expressed as $-\Delta S_M^\text{max} \propto B$.

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