On the crystal structure and magnetic properties of the Mn 0.94Ti0.06CoGe alloy

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On the crystal structure and magnetic properties of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy

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Structural and magnetic properties of Mn$_{0.94}$Ti$_{0.06}$CoGe have been studied by a combination of bulk magnetisation and neutron diffraction measurements over the temperature range of 5 K–350 K. The crystal structural transition occurs at $T_{str}$ (~235 K) with a change in symmetry from the low temperature orthorhombic TiNiSi-type structure (space group Pnma) to the high temperature hexagonal Ni$_2$In-type structure (space group P6$_3$/mmc) and the magnetic phase transition takes place around $T_C$ = 270 K. It is found that the structural transition around $T_{str}$ is incomplete and there is a co-existence of the orthorhombic and hexagonal structures between $T_{str}$ and $T_C$ (~270 K). These results are discussed in connection with the magnetic and magnetocaloric behaviours in Mn$_{0.94}$Ti$_{0.06}$CoGe.

Materials which experience simultaneous crystallographic and magnetic phase transitions have garnered a lot of interest owing to their promising applications as multifunctional materials.\cite{1,2,3} Recently, it has been reported that this magnetostructural coupling in the MnCoGe-based materials can lead to a large magnetocaloric effect (MCE)\cite{4,5} around room temperature. Thus, the MnCoGe-related systems exhibit great potential to be used as refrigerants in magnetic refrigeration (MR). MR is regarded as a promising, environmentally friendly, and more efficient alternative to the currently used conventional gas-compression based refrigeration.\cite{6} Up to now, a lot of studies have been done on the tuning of the interatomic distances resulting in the transformation in enhancing the magnetic entropy change, we performed a temperature dependent neutron diffraction experiment over the temperature range of 5–350 K. In this work, we present our comprehensive neutron diffraction investigation of Mn$_{0.94}$Ti$_{0.06}$CoGe alloy.

Details of the sample preparation methods and experimental procedures have been presented elsewhere.\cite{12} Around 1 g powder sample of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy was placed in a vanadium sample holder, which was then fitted inside a cryocooler and then mounted on the sample stage of the diffractometer for the neutron diffraction measurements. The neutron data were collected in the temperature range of 5–350 K at the high intensity powder diffractometer, Wombat at OPAL with an incident neutron wavelength of $\lambda = 2.4177$ Å. To determine the structural parameters, the neutron diffraction patterns were analysed using Rietveld\cite{13,14} refinements with the FULLPROF package.

A temperature dependent neutron diffraction image for selected 20 region is shown in Fig. 1 with the orthorhombic phase (hkl) Miller indices (space group Pnma) being marked without * and the hexagonal phase (hkl) Miller indices (space group P6$_3$/mmc) with *.

We have recently investigated the effects of the substitution of Ti into Mn$_{1-x}$Ti$_x$CoGe compounds, with the best sample from that study, the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy, exhibiting a giant magnetocaloric effect. Results on the magnetic and magnetocaloric properties as well as the critical behavior of the Mn$_{0.94}$Ti$_{0.06}$CoGe alloy have been presented elsewhere.\cite{12} In order to probe further the magnetostructural coupling and fully understand the role of structural and magnetic transformation in enhancing the magnetic entropy change, we performed a temperature dependent neutron diffraction experiment over the temperature range of 5–350 K. In this work, we present our comprehensive neutron diffraction investigation of Mn$_{0.94}$Ti$_{0.06}$CoGe alloy.

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FIG. 1. Neutron diffraction image for Mn$_{0.94}$Ti$_{0.06}$CoGe taken at 5K steps over the temperature range of 5–350 K.
increasing temperature one structure transition takes place starting from around 220 K and completing at 270 K, which agrees well with our magnetic study measurements (not shown here) revealing a phase transition at approximately 235 K. Compared with the parent MnCoGe compound, where the structure change occurring at $T_{str} \approx 650$ K, the substitution of 6% Ti for Mn leads to a significant reduction in $T_{str}$. In order to show the transition clearly, we draw the neutron diffraction patterns at selected temperatures ($T = 200$ K, 245 K, and 350 K) in Figure 2(a).

It can be seen from Fig. 2(a) that at 200 K the compound crystallizes in the orthorhombic TiNiSi-type structure (space group Pnma), while at 350 K the crystal structure changes to the hexagonal Ni$_2$In-type (space group P6$_3$/mmc). At 245 K, there is a co-existence of both phases, thus confirming our expectations from magnetic measurements. Further analysis of the neutron diffraction data using the Rietveld refinement resulted in the determination of the lattice parameters as well as the volume phase fractions for the orthorhombic and hexagonal phases. Fig. 2(b) shows the evolution of the orthorhombic and hexagonal phase fractions as a function of temperature. The volume phase fractions as a function of temperature have been fitted using the sigmoidal Boltzmann equation shown in the following equation:

$$F(T) = \left( F(T_1) - F(T_2) \right) \left( 1 + \exp \left[ \frac{T - T_{str}}{dF} \right] + F(T_2) \right).$$ (1)

The orthorhombic and hexagonal phase fractions represented by the fitting coefficients $F(T_1)$ and $F(T_2)$ are 98.8 and 6.99 as well as 1.2 and 93.01 vol. %, respectively. The orthorhombic phase fraction determined from the neutron diffraction pattern measured at 5 K is approximately 100 vol. %, which is in excellent agreement with the $F(T_1)$ value of 98.8 ± 1.59 determined from the sigmoidal Boltzmann fit.

The peak intensities of the selected reflections (002)$^*$ (for P6$_3$/mmc) and the (011) (for Pnma) as a function of temperature are shown in Fig. 2(c). The peak intensity of the (011) reflection which decreases with an increase in temperature corresponds to the decrease of the Pnma phase fraction, whilst the peak intensity of the (002)$^*$ reflection which increases with an increase in temperature corresponds to the increase of the P6$_3$/mmc phase fraction with temperature.

Fig. 3 shows the refined structural parameters of the Mn$_{0.94}$Ti$_{0.06}$CoGe compound as a function of temperature from neutron diffraction data. The lattice parameters and
Previous electronic structure calculations for MnCoGe show splitting of the majority and minority bands consequently resulting in its larger saturation moment. In the hexagonal phase, the shorter Mn-Mn distances strengthen the exchange coupling leading to broader 3d band width. So, the observed giant MCE around T_{str} (approximately 18 J/kg K for ΔB = 8 T) in the Mn_{0.93}Ti_{0.06}CoGe compound can be attributed to the combined effect of an abrupt change in magnetization as well as volume in the vicinity of the structural transition (structural entropy change).

The lattice parameters as well as volume phase fractions for the orthorhombic and hexagonal phases of the Mn_{0.93}Ti_{0.06}CoGe alloy have been determined from neutron powder diffraction data measured in the temperature range of 5–350 K using Rietveld refinement. The volume phase fractions as a function of temperature were fitted using the sigmoidal Boltzmann equation and the numerical coefficients F(T_1) and F(T_2) representing the fitted orthorhombic and hexagonal phase fractions at T_1 = 0 K and T_2 = +∞ were determined. A large volume change ΔV/V = 3.45% was detected at the structural transition T_{str} ~ 235 K with a significant drop in magnetization being observed. Both changes in crystal structure and magnetization around T_{str} are found to contribute to the larger magnetocaloric effects determined.

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[Fig. 4. Field dependences of magnetization of the Mn_{0.93}Ti_{0.06}CoGe compound showing the drop in magnetization in the vicinity of T_{str}.]