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

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Structural and magnetic properties of $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ 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_2In -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 $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$. © 2013 AIP Publishing LLC [<http://dx.doi.org/10.1063/1.4801523>]

Materials which experience simultaneous crystallographic and magnetic phase transitions have garnered a lot of interest owing to their promising applications as multifunctional materials.^{1–3} Recently, it has been reported that this magnetostructural coupling in the MnCoGe -based materials can lead to a large magnetocaloric effect (MCE)^{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.⁶ Up to now, a lot of studies have been done on the tuning of the magnetostructural coupling in the MnCoGe system.^{4,5,7} The parent MnCoGe compound is a ferromagnet with a Curie temperature $T_C \sim 345$ K, which crystallizes in the orthorhombic TiNiSi -type crystal structure (space group $Pnma$) at room temperature and undergoes a diffusionless crystallographic phase transition to the high temperature hexagonal Ni_2In -type structure (space group $P6_3/mmc$) on heating at the structural transition temperature, $T_{\text{str}} \sim 650$ K.^{5,8–11} In order to modify the interatomic distances resulting in the tuning of the magnetostructural coupling in MnCoGe compound, several different ways such as substitutions, dopings, and the application of physical pressure have been used.^{4,5,7}

We have recently investigated the effects of the substitution of Ti into $\text{Mn}_{1-x}\text{Ti}_x\text{CoGe}$ compounds, with the best sample from that study, the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy, exhibiting a giant magnetocaloric effect. Results on the magnetic and magnetocaloric properties as well as the critical behavior of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy have been presented elsewhere.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 $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy.

Details of the sample preparation methods and experimental procedures have been presented elsewhere.¹² Around 1 g powder sample of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ 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^{13,14} refinements with the FULLPROF package.

A temperature dependent neutron diffraction image for selected 2θ 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 *. It can be seen clearly that with

FIG. 1. Neutron diffraction image for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ taken at 5 K steps over the temperature range of 5–350 K.

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FIG. 2. (a) Neutron diffraction patterns at 200 K, 245 K, and 350 K. (b) Quantitative phase analysis of the orthorhombic TiNiSi -type phase (space group *Pnma*) and the hexagonal Ni_2In -type phase (space group *P6₃/mmc*). (c) The peak area as a function of temperature for the (002)* and (011) peaks.

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.¹² Compared with the parent MnCoGe compound, where the structure change occurring at $T_{\text{str}} \sim 650$ 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_2In -type (space group *P6₃/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:

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

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 *P6₃/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 *P6₃/mmc* phase fraction with temperature.

Fig. 3 shows the refined structural parameters of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ compound as a function of temperature from neutron diffraction data. The lattice parameters and

FIG. 3. Volume and lattice parameters as a function of temperature. Open symbols denote the orthorhombic phase, closed symbols denote the hexagonal phase, and half-filled symbols denote the corresponding phases in the mixed phase region.

FIG. 4. Field dependences of magnetization of the $Mn_{0.94}Ti_{0.06}CoGe$ compound showing the drop in magnetization in the vicinity of T_{str} .

volumes between these two structures can be described by $a = a_{ortho} = c_{hex}$, $b = b_{ortho} = a_{hex}$, $c = c_{ortho} = \sqrt{3}a_{hex}$, and $V = V_{ortho} = 2V_{hex}$.^{15,16} The lattice parameter b indicates the exchange interaction between the Mn-Mn moments along this axis and a change in this parameter strongly influences the Curie temperature. Around the structural transition temperature, $T_{str} \sim 235$ K, it is clearly evident in Fig. 3 that when the symmetry changes from orthorhombic to hexagonal, there is a large volume change ($\Delta V = 1/2V_{orth} - V_{hex} = 2.65 \text{ \AA}^3$ so approximately $\Delta V/V = 3.45\%$). By comparison, Kanomata *et al.*⁹ estimated the difference in the unit cell volume at T_{str} $\Delta V \sim 3 \text{ \AA}^3$ for the $MnCoGe$ alloy. For first order magnetic phase transitions, it is assumed that the total field-induced magnetic entropy change ΔS_{tot} can be expressed as the sum of the conventional second-order magnetic entropy change (ΔS_M) and the entropy differences of the two different crystallographic polymorphs (ΔS_{st}), i.e., $\Delta S_{tot} = \Delta S_M + \Delta S_{st}$. It was reported that the structural entropies are proportional to the volume differences of the phases involved in the transition.¹⁷ Such a difference in the volume change around T_{str} for $Mn_{0.94}Ti_{0.06}CoGe$ will lead to a significant structural entropy change then resulting in the total magnetic entropy change.

Moreover, around T_{str} the closest distance between Mn-Mn is determined to be $2.985 \text{ \AA}$ in the $TiNiSi$ -type unit-cell, while it changes to $2.651 \text{ \AA}$ in the Ni_2In -type unit-cell. The bond lengths were calculated using the BLOKJE program.¹⁸ According to Goodenough's theory, which explains the localized character of the magnetic moment in alloys, in the $Mn_{0.94}Ti_{0.06}CoGe$ compound, the moment is carried by the Mn and Co atoms.¹⁹ At 5 K, the calculated saturation moments μ_{Mn} and μ_{Co} are 2.86 and $1.63 \mu_B$, respectively, with $\mu_{Mn} = 2.76$ and $\mu_{Co} = 1.68 \mu_B$ at 200 K. At 200 K in the $TiNiSi$ -type unit-cell, the closest distance between Mn-Mn is $2.984 \text{ \AA}$, while at 345 K in the Ni_2In -type unit-cell the closest distance between Mn-Mn changes to $2.658 \text{ \AA}$. In this work, the quality of the obtained neutron data was such that the calculated magnetic moment for the hexagonal phase was unreliable. If we assume that the magnetic moments for Mn and Co atoms for the Pnma phase do not change between 200 K and 245 K, the derived values of μ_{Mn} and μ_{Co} for $P6_3/mmc$ at 245 K are 1.0 and $1.3 \mu_B$, respectively. The reduction of the saturation moment is expected in the hexagonal phase compared with the orthorhombic phase.²⁰ Fig. 4 shows the sudden drop of magnetization in the vicinity of T_{str} . Previous electronic structure calculations for $MnCoGe$ show that the larger Mn-Mn distance in the orthorhombic phase is consistent with a narrower $3d$ band width and a larger exchange

splitting between 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.^{20,21} So, the observed giant MCE around T_{str} (approximately 18 J/kg K for $\Delta B = 8 \text{ T}$) in the $Mn_{0.94}Ti_{0.06}CoGe$ 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 $Mn_{0.94}Ti_{0.06}CoGe$ 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 $T_1 = 0 \text{ K}$ and $T_2 = +\infty$ were determined. A large volume change $\Delta V/V = 3.45\%$ was detected at the structural transition $T_{str} \sim 235 \text{ K}$ 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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