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The magnetocaloric effect and critical behaviour of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy

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Abstract

Structural, magnetic and magnetocaloric properties of the Mn_{0.94}Ti_{0.06}CoGe alloy have been investigated using x-ray diffraction, DC magnetization and neutron diffraction measurements. Two phase transitions have been detected, at $T_{\text{str}} = 235$ K and $T_{\text{C}} = 270$ K. A giant magnetocaloric effect has been obtained at around T_{str} associated with a structural phase transition from the low temperature orthorhombic TiNiSi-type structure to the high temperature hexagonal Ni₂In-type structure, which is confirmed by neutron study. In the vicinity of the structural transition, at T_{str} , the magnetic entropy change, $-\Delta S_{\text{M}}$ reached a maximum value of $14.8 \text{ J kg}^{-1} \text{ K}^{-1}$ under a magnetic field of 5 T, which is much higher than that previously reported for the parent compound MnCoGe. To investigate the nature of the magnetic phase transition around $T_{\text{C}} = 270$ K from the ferromagnetic to the paramagnetic state, we performed a detailed critical exponent study. The critical components γ , β and δ determined using the Kouvel-Fisher method, the modified Arrott plot and the critical isotherm analysis agree well. The values deduced for the critical exponents are close to the theoretical prediction from the mean-field model, indicating that the magnetic interactions are long range. On the basis of these critical exponents, the magnetization, field and temperature data around T_{C} collapse onto two curves obeying the single scaling equation $M(H, \epsilon) = \epsilon^{\beta} f_{\pm}(H/\epsilon^{\beta+\gamma})$.

Keywords

mn0, effect, behaviour, magnetocaloric, 94ti0, 06coge, alloy, critical

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Magnetocaloric effect and Critical behavior in the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy

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Abstract

Structural, magnetic and magnetocaloric properties of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy have been investigated using x-ray diffraction, DC magnetization and neutron diffraction measurements. Two phase transitions have been detected at $T_{\text{str}} = 235$ K and $T_{\text{C}} = 270$ K, respectively. A giant magnetocaloric effect has been obtained around T_{str} associated with a structural phase transition from the low temperature orthorhombic TiNiSi -type structure to the high temperature hexagonal Ni_2In -type structure, which is confirmed by neutron study. In the vicinity of the structural transition, T_{str} , the magnetic entropy change, $-\Delta S_{\text{M}}$ reached a maximum value of $14.8 \text{ J kg}^{-1} \text{ K}^{-1}$ under a magnetic field of 5T which is much higher than that previously reported on the parent compound MnCoGe . To investigate the nature of the magnetic phase transition around $T_{\text{C}} = 270$ K from ferromagnetic to paramagnetic state, we performed a detailed critical exponent study. The critical components, γ , β and δ determined using the Kouvel-Fisher method, the modified Arrott plot as well as the critical isotherm analysis agree well. The values deduced for the critical exponents are close to the theoretical prediction of the mean-field model, indicating that the magnetic interactions are long range. Based on these critical exponents, the magnetization, field and temperature data around T_{C} collapse into two curves obeying the single scaling equation $M(H, \varepsilon) = \varepsilon^{\beta} f_{\pm}(H / \varepsilon^{\beta+\gamma})$.

1. Introduction

In the last years, there has been a considerable increase in research on near room temperature magnetic cooling¹⁻⁵. This new cooling technology, which is expected to supersede the conventional refrigeration technology based on gas-compression/expansion, is of special interest because of its considerable socio-economic benefits. Compared to the refrigeration technology based on gas-compression/expansion, which is widely used today, magnetic refrigeration is environmentally friendly and more efficient^{2,6}. The magnetic refrigeration is based on the magnetocaloric effect (MCE), which results from the coupling of a system of magnetic moments with an external magnetic field resulting in the cooling or heating of a

system⁷. Material systems such as LaFeSi⁷, NiMnGa⁸, MnAsSb⁹, GdSiGe¹⁰ undergo first order magnetic transitions and have been found to possess giant MCE. However, some major drawbacks of these material systems includes large thermal and magnetic hysteresis which are detrimental to the refrigerant capacity, and thus undesirable for practical applications. Hence, it is imperative to search for materials that exhibit giant MCE as well as negligible thermal and magnetic hysteresis. One candidate is MnCoGe^{11 - 14} which undergoes a second order phase transition as well as a crystallographic phase transition from the low temperature orthorhombic TiNiSi type to the high temperature hexagonal Ni₂In type structure¹⁵. Previously, scientists have managed to achieve a coupling of the magnetic and crystallographic transitions in the MnCoGe material system by substitution of Cr¹⁶ and by the addition of boron^{17 - 18} as an interstitial thereby leading to the attainment of a giant magnetocaloric effect.

We have investigated the substitution of Ti into Mn_{1-x}Ti_xCoGe compounds with $x = 0.02$, 0.04 and 0.06 and we found that for the, $x = 0.06$ substitution most successfully shifted the structural change and magnetic phase transition into our interested temperature range leading to the attainment of a giant magnetocaloric effect. In this paper, we focus on the magnetic properties and critical behaviour of the Mn_{0.94}Ti_{0.06}CoGe alloy. Thus in an effort to understand the nature of the magnetic transition in Mn_{0.94}Ti_{0.06}CoGe, we performed a critical exponent analysis in the vicinity of the ferromagnetic (FM) - paramagnetic (PM) region^{19 - 21}. To date, to the best of our knowledge, no experimental study of the critical phenomena has been reported for the MnCoGe - based system. Our results reveal that this material undergoes a structural transition at ~ 235 K as well as a second order ferromagnetic – paramagnetic transition at ~ 270 K. Furthermore, we performed a temperature dependent neutron diffraction experiment to clarify whether there exists a coupling of the structural transition and the magnetic phase transition.

2. Experimental details

Polycrystalline Mn_{1-x}Ti_xCoGe ($x = 0, 0.02, 0.04$ and 0.06) ingots were prepared by arc melting the appropriate amounts of Mn (99.9%), Ti (99.999%) powder, Co (99.9%) and Ge (99.999%) chips in an argon atmosphere. During arc melting, a 3% excess Mn over the stoichiometric amount was added to compensate the weight loss of Mn. The polycrystalline ingots were melted five times to achieve good homogeneity. The ingots were then wrapped in tantalum foil, sealed in a quartz ampoule and subsequently annealed at 850 °C for 120 hours

and then quenched in water at room temperature. The magnetization measurements were carried out using the vibration sample magnetometer option of a Quantum Design 14 T Physical Property Measurement System (PPMS) and a Quantum Design Physical Property Measurement System (MPMS) in the temperature range of 100 – 340 K at applied fields of up to 5 T. For critical exponent study, magnetization isotherms were measured in the temperature range 249 – 299 K with an interval of 2 K at applied fields of up to 5 T. The neutron data was collected in the temperature range 5 – 340 K at the high intensity powder diffractometer, *Wombat* at OPAL with an incident neutron wavelength of $\lambda = 2.4177 \text{ \AA}$.

3. Results and Discussion

3.1. Magnetic phase transitions

Temperature dependence [100 K to 340 K] of the magnetization of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy measured in a magnetic field of $\mu_0 H = 0.01 \text{ T}$ is shown in Fig. 1. The sample was measured on warming in a field of $\mu_0 H = 0.01 \text{ T}$ after first cooling in zero field (marked as ZFC). The field-cooled cooling magnetization curve, FC, was then recorded on cooling from 340 K to 5 K in an applied field of $\mu_0 H = 0.01 \text{ T}$. A decoupling of the structural and magnetic transitions is clearly observed in the M-T curve as a two-step transition, which was later confirmed by neutron experiment. Bayreuther *et al.* showed that T_C determined from the linear extrapolation of $M^2 (T)$ to $M = 0$ as suggested by the molecular field theory yields a value closer to the true transition temperature as opposed to the T_C determined from the minimum of dM/dT ²². The inset shows a plot of M^2 vs T, which reveals a magnetic transition from FM to PM at the ordering temperature, $T_C \sim 270 \text{ K}$ as well as a plot of dM/dT showing the structural transition at $T_{\text{str}} \sim 235 \text{ K}$. The absence of thermal hysteresis in the vicinity of the magnetic PM to FM transition is a clear evidence of the second order nature of this transition. However, a notable thermal hysteresis is observed in the vicinity of the magneto-structural transition from the antiferromagnetic TiNiSi -type to the ferromagnetic Ni_2In -type structure confirming its first order nature. It has been previously established that the presence of a small hysteresis at T_{str} is indicative of a magnetoelastic character at the FM to AFM transition¹⁷.

3.2. Magnetocaloric effect

In an isothermal process, the magnetic entropy change of the materials can be derived from the Maxwell relation as shown below:

$$\Delta S_M(T, p, \Delta H)_{\Delta H, p} = \int_{H_1}^{H_2} \left[\frac{\partial M(T, p, H)}{\partial T} \right]_{H, p} dH \quad (2)$$

The magnetic entropy changes, ΔS_M of materials have been calculated using the Maxwell relation²³ and shown in Fig. 2 (a) as a function of temperature and field. Although the use of Maxwell's relation for 1st order systems is still questionable, Caron *et al.* successfully established a method of determining the magnetic entropy change of 1st order systems by using the decreasing field²⁴. In our work, we have also evaluated the magnetic entropy change, ΔS_M in the decreasing field mode, which is shown by the dotted curves in Fig 2(a). A comparison of the ΔS_M values calculated using increasing and decreasing fields respectively shows that the difference between these values is very small, which confirms that there is negligible hysteresis loss occurring in the vicinity of the structural transition thus demonstrating the applicability of the Maxwell relation. As expected, $-\Delta S_M$ increases with the increase in the applied magnetic field. The inset showing the variation of the magnetic entropy with temperature at 1 T, clearly displays two maxima, one occurring at the structural transition and the other at the magnetic transition. Interestingly, the maximum magnetic entropy change is found to be in the vicinity of $T_{str.}$ and is about $-11.3 \text{ Jkg}^{-1}\text{K}^{-1}$ for a magnetic field change ΔB of 5 T, which is about one order of magnitude higher than that found in the undoped MnCoGe ($\approx 4.8 \text{ Jkg}^{-1}\text{K}^{-1}$ at 5 T)¹⁷. Around the FM to PM transition temperature T_C , $-\Delta S_M$ is found to be about $3 \text{ Jkg}^{-1}\text{K}^{-1}$ for a magnetic field change ΔB of 5 T. The difference of $-\Delta S_M$ at $T_{str.}$ and T_C can be understood in the terms of the difference in the order of phase transitions. Compared with some alloys with second order magnetic transition, the $-\Delta S_M$ peak in $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ is comparable to that in Gd^{25} ($\approx 10.2 \text{ Jkg}^{-1}\text{K}^{-1}$ at 5 T). Fig 2 (b) shows the dependence of the magnetic entropy change on the parameter $(\mu_0 H/T_C)^{2/3}$. The mean field theory predicts that in the vicinity of second-order phase transitions, ΔS_M is proportional to $(\mu_0 H/T_C)^{2/3}$ ^{26 - 27}. The linear fit to the data in figure 2(b) clearly demonstrates that the relationship $\Delta S_M \propto (\mu_0 H/T_C)^{2/3}$ is valid around T_C .

As shown by neutron diffraction study in Fig. 3, the phase transition at T_{str} includes the changes in both the crystal symmetry and magnetic properties. The change of symmetry is from the low-temperature orthorhombic TiNiSi -type structure (space group $Pnma$) to the high-temperature hexagonal Ni_2In -type structure (space group $P63/mmc$) while the change of

magnetic properties are related to the difference of the magnetic moment for these two phases. For the parent MnCoGe compound it was found that in the hexagonal structure, the values of the saturation moment, M_S is $2.76 \mu_B$ while in the orthorhombic structure with a higher $M_S = 4.13 \mu_B$ ²⁸. Therefore, the entropy changes around T_{str} includes both magnetic and structural contribution while the ΔS_M around T_C only includes the magnetic entropy change. Moreover, it was found from Fig. 3 that the structural transition around T_{str} is not complete. There is a coexistence of the orthorhombic and hexagonal structures below T_C . The phase fraction is shown as an inset in Fig. 3. The details of refinement for neutron patterns will be presented elsewhere²⁹. From the crystallographic point of view, the TiNiSi-type unit-cell can be considered as an orthorhombic distortion of the hexagonal Ni₂In-type unit-cell. However, the chemical environment has a significant change after the structure change. For example, at $T = 235$ K where the phase fraction is 65.3% for Pnma and 34.7 % for P63/mmc. In the TiNiSi-type unit-cell, the closest distance between Mn-Mn is $2.985 \text{ \AA}$ while in the Ni₂In-type unit-cell it changes to $2.651 \text{ \AA}$.

3.3. Critical exponent analysis

In an effort to further clarify the nature of the FM – PM phase transition, we performed an analysis of the critical behaviour near T_C . We measured the isothermal magnetization versus the applied field around T_C using an interval of 2 K as shown in Fig. 4(a). A plot of H/M versus M^2 , known as the standard Arrott plot, is shown in Fig. 4(b) for the temperatures in the vicinity of T_C . According to the criterion proposed by Banerjee³⁰, the order of magnetic transition can be determined from the slope of the isotherm plot. If the H/M versus M^2 curves show a negative slope, the transition is first order while a positive slope corresponds to a second order transition. For the Mn_{0.94}Ti_{0.06}CoGe alloy, the positive slope of the H/M versus M^2 curves throughout the transition temperature indicates that the phase transition is second order. This result is consistent with the absence of thermal hysteresis in the vicinity of the PM – FM transition as shown in Fig. 1, thereby confirming the second order nature of this transition. However, a close inspection of the H^2 versus M^2 curves reveals that all the curves are not parallel to each other (see the parallel dashed lines in Fig. 4(b)), indicating that the critical exponents of $\beta = 0.5$ and $\gamma = 1$ are not satisfied. The scaling hypothesis postulates that a second order magnetic phase transition near T_C is characterized by a set of critical exponents namely, β , γ and δ ³¹. In this work, we have used different methods to investigate the critical behaviour of the Mn_{0.94}Ti_{0.06}CoGe alloy, namely the modified Arrott plots

(MAPs), Kouvel-Fisher method, critical isotherm analysis and the Widom scaling relation. The first method used to calculate the critical exponents is the MAPs method, which is based on the Arrott-Noakes equation of state³². Quantitative fits are made to the Arrott plots using the following equations³³.

$$M_S(T) = \lim_{H \rightarrow 0}(M) = M_0 (-\varepsilon)^\beta, \varepsilon < 0 \quad (2)$$

$$\chi_0^{-1}(T) = \lim_{H \rightarrow 0}(H/M) = (h_0/M_0)\varepsilon^\gamma, \varepsilon > 0 \quad (3)$$

where M_0 and h_0 are constants and $\varepsilon (= (T-T_C)/T_C)$ is the reduced temperature. Initial values of β and γ are selected, then a plot of $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$ is obtained. M_S is then determined from the intersection of the linearly extrapolated curve with the $M^{1/\beta}$ axis. It is imperative to note that only the high field linear region is used for the analysis because MAPs tend to deviate from linearity at low field due to the mutually misaligned magnetic domains³⁴. Next, M_S is plotted as a function of temperature. To determine $\chi_0^{-1}(T)$ a similar procedure is used in conjunction with the $(H/M)^{1/\gamma}$ axis. The values of $\chi_0^{-1}(T)$ and $M_S(T)$ are plotted as a function of temperature in Fig. 4(c) and these plots are then fitted with equations (2) and (3), thus obtaining values of β and γ . These new critical exponent values are then used to construct new MAPs. These steps are repeated until the iterations converge to the optimum β , γ and T_C values. Using equations (2) and (3), the MAPs shown in Fig. 4(c) yielded critical parameters, $\beta = 0.61 \pm 0.04$ and $\gamma = 0.91 \pm 0.02$. The modified Arrott plots are drawn in Fig. 4(d) which shows clearly that all lines are parallel to each other (dashed lines as an eye guide),

The Kouvel-Fisher method which makes use of the equations (4) and (5) shown below, is a more accurate way of determining the critical exponents β and γ ³⁵

$$\frac{M_S(T)}{\frac{dM_S(T)}{dT}} = \frac{T - T_C}{\beta} \quad (4)$$

$$\frac{\chi_0^{-1}(T)}{d\chi_0^{-1}(T)/dT} = \frac{T - T_C}{\gamma} \quad (5)$$

According to the equations (4) and (5), plotting $M_S(T)[dM_S/dT]^{-1}$ and $\chi_0^{-1}(T)[d\chi_0^{-1}/dT]^{-1}$ versus temperature yields straight lines with slopes of $1/\beta$ and $1/\gamma$ respectively as shown in Fig 5(a). The value of T_C is obtained from the intercepts on the x -axis. The critical exponents β and γ as well as T_C obtained using the Kouvel-Fisher method are $\beta = 0.61 \pm 0.04$, $T_C = 276$ K and $\gamma = 0.91 \pm 0.03$, $T_C = 275$ K. A comparison of the critical exponents β and γ obtained using the MAPs and those obtained using the KF method reveals that these values match extremely well.

The value of the critical component δ can be determined directly from the critical isotherm $M(T_C, H)$ according to equation (6) below.

$$M_{T_C} = DH^{1/\delta}, \varepsilon = 0, T = T_C \quad (6)$$

Fig. 5(b) shows the magnetic field dependence of magnetization at $T_C = 275$ K for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy. The insert shows the critical isotherm on a log – log scale. From equation (6) a plot of $\log(M)$ versus $\log(H)$ is expected to be a straight line with slope $1/\delta$. The obtained δ value from the critical isotherm is 2.59. Another way of obtaining the critical component δ is by using the Widom scaling relation shown in equation (7):

$$\delta = 1 + \frac{\gamma}{\beta} \quad (7)$$

Using equation (6) and the critical parameters β and γ obtained using the MAPs and those obtained using the Kouvel-Fisher method, the deduced δ values are 2.52 and 2.49 respectively. Thus, the Widom scaling relation has confirmed the reliability of the critical exponents deduced from the experimental data.

The reliability of the calculated exponents β and γ can be confirmed by using the scaling theory. In the critical region, according to the scaling theory, the magnetic equation of state can be written as:

$$M(H, \varepsilon) = \varepsilon^\beta f_\pm(H/\varepsilon^{\beta+\gamma}) \quad (8)$$

Where ε is the reduced temperature $(T - T_C) / T_C$ and f_+ and f_- are regular analytical functions above and below T_C respectively. Using β and γ obtained from the Kouvel-Fisher method, the plots of M / ε^β versus $H / \varepsilon^{(\beta+\gamma)}$ (shown in Fig. 5(c)) yield two universal curves, one for temperatures above T_C and the other one for temperatures below T_C , in agreement with the scaling theory. This therefore confirms that the obtained values of the critical components as well as the T_C are reliable and in agreement with the scaling hypothesis.

It is well accepted that the order parameter of phase transition around magnetic transition temperature is fluctuating on all available length scales and those fluctuations smear out the microscopic details of the interactions in the continuous phase transition system³⁶. The mean field interaction model for long range ordering has theoretical critical exponents of $\beta = 0.5$, $\gamma = 1.0$ and $\delta = 3.0$ ³⁷ while the theoretical values based on the three dimensional Heisenberg model corresponding to short range interactions are $\beta = 0.365$, $\gamma = 1.386$ and $\delta = 4.80$ ³⁸. The δ , β , γ values derived for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy are close to the mean field values, thus indicating that long range interactions dominate the critical behavior around T_C in this compound. Thus, the critical behaviour analysis in the vicinity of T_C determined that the magnetism of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy is governed by long range interactions, which is in agreement with the linear fit to the data in figure 2(b) which clearly demonstrates that the relationship $\Delta S_M \propto (\mu_0 H / T_C)^{2/3}$ is valid around T_C .

4. Conclusions

A giant MCE associated around 235 K has been observed for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy which has been found to be related to a first-order structural transformation. The giant MCE values are comparable with those reported for materials that exhibit a giant MCE in this temperature range. An excellent agreement of the critical exponents of the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy determined using the isothermal magnetization in the vicinity of T_C based on various techniques such as the Kouvel-Fisher method, the modified Arrott plot as well as the critical

isotherm was obtained. Moreover, all critical exponents fulfil the Widom scaling law. The validity of the calculated critical components was confirmed by the scaling equation with the obtained magnetization, field and temperature data below and above T_C collapsing into two different curves. Thus, the scaling of the magnetization data above and below T_C obtained using the respective critical exponents and the consistency in the values of the critical exponents determined by different methods confirm that our calculated exponents are unambiguous and intrinsic. The determined critical exponents are close to those predicted by the mean-field theory, with long range interactions.

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Figure captions:

FIG. 1. Temperature dependence of magnetization. The inset shows dM/dT vs T used for the determination of T_{str} as well as M^2 vs T used for the determination of T_C .

FIG. 2. (a) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M(T, H)$ for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ calculated from magnetization isotherms; (b) Dependence of the magnetic entropy change on the parameter $(\mu_0 H / T_C)^{2/3}$. The solid line represents a linear fit to the data.

FIG. 3. Neutron diffraction patterns over the temperature range 10 – 340 K at 10 K intervals. Below T_{str} and above T_C , the neutron pattern can be indexed well with the space group Pnma (orthorhombic structure - hkl Miller indices without*) and space group P63/mmc (hexagonal - hkl Miller indices with*), respectively. Between T_{str} and T_C , the pattern indicates the coexistence of the orth. phase and the hex. phase.

FIG. 4. (a) Isothermal magnetization curves for $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ in the vicinity of T_c ; (b) Arrott plot of M^2 vs H / M at temperatures in the vicinity of T_c ; (c) Temperature dependence of the spontaneous magnetization M_s and inverse initial susceptibility χ_0^{-1} (solid lines are fitted to equations (2) and (3)); (d) Modified arrott plot obtained by the Kouvel - Fisher method showing isotherms of $M^{1/\beta}$ vs $(\frac{H}{M})^{1/\gamma}$ with the calculated $\beta = 0.61$ and $\gamma = 0.91$.

FIG. 5. (a) Kouvel-Fisher plot for the spontaneous magnetization $M_S(T)$ and the inverse initial susceptibility $\chi_0^{-1}(T)$ (solid lines are fitted to equations (4) and (5)); (b) The critical isotherm analysis at T_C . The inset shows the same plots on the log – log scale (solid line is a linear fit to equation (6)); (c) Scaling plots indicating universal curves below and above T_C for the $\text{Mn}_{0.94}\text{Ti}_{0.06}\text{CoGe}$ alloy.