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Ti substitution for Mn in MnCoGe - The magnetism of Mn0.9Ti0.1CoGe

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Abstract

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Ti substitution for Mn in MnCoGe – The magnetism of $Mn_{0.9}Ti_{0.1}CoGe$

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Bulk magnetization measurements (5 - 320 K; 0 – 8 T) reveal that below room temperature $Mn_{0.9}Ti_{0.1}CoGe$ exhibits two magnetic phase transitions at ~178 K and ~280 K. Neutron diffraction measurements (3 – 350 K) confirm that the transition at ~178 K is due to the structural change from the low-temperature orthorhombic TiNiSi-type structure (space group Pnma) to the higher temperature hexagonal Ni_2In-type structure (space group P63/mmc), while the transition at ~280 K originates from the transition from ferromagnetism to paramagnetism. The magnetocaloric behaviour of $Mn_{0.9}Ti_{0.1}CoGe$ around T_{str}~178 K and T_C~280 K as determined *via* the magnetic field and temperature dependences of DC magnetisation are given by the maximum values of the magnetic entropy changes $-\Delta S_M^{max} = 6.6$ J kg^{-1} K^{-1} around T_{str}~178 K, and $-\Delta S_M^{max} = 4.2$ J kg^{-1} K^{-1} around T_C~280 K for a magnetic field change of ΔB=0-8 T. Both structural entropy - due to the unit cell expansion of ~4.04% - and magnetic entropy - due to an increase in the magnetic moment of ~31% - are

found to contribute significantly to the total entropy change around T_{str}. Critical analysis of the transition around $T_C \sim 280$ K leads to exponents similar to values derived from a mean field theory, consistent with long-range ferromagnetic interactions. It was found that the field dependence of $-\Delta S_M^{max}$ can be expressed as $-\Delta S_M^{max} \propto B^n$ with n=1 for the structural transition around T_{str} and n=2/3 for the ferromagnetic transition around T_C, thereby confirming the second order nature of this latter transition.

Introduction

Magnetic refrigeration (MR) based on the magnetocaloric effect (MCE) offers an environmentally friendly cooling technology with relatively high energy efficiency [1, 2]. Depending on the temperature of maximum entropy change, materials which exhibit a large magnetocaloric effect offer scope for magnetic refrigeration at cryogenic temperatures and around room temperature; as such they continue to attract significant interest and attention [e.g. 3, 4]. Materials with first-order magnetic phase transitions (FOMT) are of particular interest as the discontinuous character of the transition can lead to intrinsically large MCE values [5-7]. Among the relatively low-cost $3d$ metal-based compounds materials whose MCE response at such FOMT has been explored are $MnAs_{1-x}Sb_x$ [7, 8], $MnFeP_{0.45}As_{0.55}$ [9], $La(Fe_{1-x}Si_x)_{13}$ and its hydrides [10, 11] as well as hexagonal MnCoGe/MnNiGe-based compounds [12, 13, 14].

Earlier studies of parent compound MnCoGe indicated that a martensitic structural transformation [15] 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) occurs at around T_{str}=650 K. [16]. The orthorhombic TiNiSi-type structure of MnCoGe is reported to be ferromagnetic below the second-order paramagnetic to ferromagnetic transition at T_c~345 K while the hexagonal Ni_2In-type structure exhibits a ferromagnetic transition at T_c~275 K [16, 17]. Given that a large volume decrease of approximately 3.9% in MnCoGe compound occurs at T_{str} when the crystal symmetry changes from orthorhombic to hexagonal [15], MnCoGe and related compounds are of interest because of the scope to control the temperatures (T_{str} an T_C to coincide or be close enough) at which the magnetic and structural transitions occur and thereby capitalise on both magnetic and structural entropies. In this way a single first-order magnetostructural transition leading to an enhanced magnetocaloric effect near room temperature can be derived [12, 13, 18]. Recently, in order to realize the desired

magnetostructural coupling, lots of efforts have been made in different ways to modify the MnCoGe/MnNGe compostions [12-13, 18-24] .

Our recent investigation [25] of $Mn_{0.94}Ti_{0.06}CoGe$ indicates that a small amount of Ti leads to a significant decrease in T_{str}; for example T_{str}=235 K for $Mn_{0.94}Ti_{0.06}CoGe$ compared with T_{str}=645 K for MnCoGe. In order to fully understand the effects of Ti substitution for Mn on the magnetic and structural properties of $Mn_{1-x}Ti_xCoGe$, here we present the results of a detailed investigation of the structural and magnetic properties of $Mn_{0.9}Ti_{0.1}CoGe$ (where both T_{str} and T_C are shifted into our interested temperature range) by dc magnetization, x-ray and neutron diffraction measurements.

Experiment process

The $Mn_{0.9}Ti_{0.1}CoGe$ sample was prepared by argon arc melting appropriate amounts of high purity elements on a water-cooled Cu hearth. Around ~3% excess Mn was used to compensate for loss during melting. The sample was re-melted five times to ensure good homogeneity and annealed at 850°C for one week in an evacuated quartz tube then quenched into water. X-ray diffraction (CuK_α) at room temperature confirmed that the sample exhibited the hexagonal Ni_2In-type structure (space group $P6_3/mmc$) with no discernible impurity phases. The magnetic measurements were carried out using a Physical Property Measurement System over the temperature range 5-320 K and at magnetic fields in the range 0-8 T. Neutron diffraction experiments were carried out over the temperature range $3 - 350$ K using the High-Resolution Powder Diffractometer Echidna ($\lambda = 1.622$ Å) at the OPAL reactor, Australia. The diffraction patterns were refined using the FULLPROF program package which allows simultaneous refinement of the structural and magnetic parameters.

Results and Discussion

Figure 1(a) shows the temperature dependence of the magnetization of $Mn_{0.9}Ti_{0.1}CoGe$ obtained at magnetic fields B=0.01 T, B=0.1 T and B=4 T. Two magnetic phase transitions can be discerned at ~178 K and ~280 K (see also the insert to Figure 1(a) which displays the B=0.01 T data on an expanded temperature range). Based on the analogous magnetic behaviour between $Mn_{0.9}Ti_{0.1}CoGe$ and $Mn_{0.94}Ti_{0.06}CoGe$ [25], these transitions can be ascribed as representing the orthorhombic to hexagonal structure at T_{str} ~ 178 K with T_C ~ 280 K indicating the paramagnetic to ferromagnetic transition in the hexagonal phase. As discussed further below, Fig. 1(a) also reveals a significant decrease in the magnetization data obtained for B=4 T around T_{str} ~ 178 K. Fig. 1(b) shows the magnetization data for $Mn_{0.9}Ti_{0.1}CoGe$ in the region of the transitions at T_{str} ~ 178 K and T_C ~ 280 K as obtained from 140 K to 320 K in 5 K increments for increasing and decreasing magnetic fields in the range B = 0- 8 T with the corresponding Arrott-plots of M^2 versus B/M shown in Fig. 1(c).

Fig. 2(a) shows the spontaneous magnetization M_s for $Mn_{0.9}Ti_{0.1}CoGe$ as a function of temperature as derived from Figs. 1(b) and 1(c). Below T_{str} in the orthorhombic phase, e.g. at T=150 K, the spontaneous magnetization M_s = 97.3 Am^2/kg corresponds to a magnetic moment of ~3.24 μ_B, while above T_{str} in the hexagonal phase, e.g. at T=200 K, the value of M_s = 67.6 Am^2/kg is equivalent to a magnetic moment of ~2.29 μ_B. These changes reflect a decrease in spontaneous magnetization M_s of about ~31% around the transition T_{str} from the orthorhombic structure to the hexagonal structure, which agrees well with the fact that the Mn and Co atoms in the TiNiSi-structure have larger magnetic moments than with Ni_2In-type based on *ab initio* total energy calculations for MnCoGe [26] and $MnCo_{1-x}Ge$ compounds [17]. Comparison of the temperature T_{str} at which the low-temperature orthorhombic structure (space group Pnma) changes to the hexagonal structure (space group P63/mmc) for the undoped MnCoGe compound [T_{str} ~ 645 K; 16], $Mn_{0.94}Ti_{0.06}CoGe$ [T_{str} ~ 235 K; 25] and $Mn_{0.9}Ti_{0.1}CoGe$ sample [T_{str} ~ 178 K; present results] demonstrates that substitution of Ti for

Mn extends the phase stability region of the hexagonal P63/mmc structure significantly to lower temperatures.

The positive slopes of the Arrott plots for $Mn_{0.9}Ti_{0.1}CoGe$ around $T_C \sim 280$ K as outlined above, Fig. 1(c), indicate that the magnetic transition around T_C is second order. According to the conventional static scaling law, the critical properties of a second-order magnetic transition can be described by critical exponents β, γ and δ derived from magnetization measurements around the transition temperature [e.g. 25, 27]. On applying these standard approaches, as shown by the fits to the Kouvel-Fisher plots of $M_s(T)(dM_s/dT)^{-1}$ and $\chi_0^{-1}(T)(d\chi_0/dT)^{-1}$ versus temperature in Fig. 2(b), the critical exponents around T_C in $Mn_{0.9}Ti_{0.1}CoGe$ have been determined to be β=0.45 and γ=0.83. Hence, on applying the relationship $\delta = 1 + \gamma/\beta$, with $\beta = 0.45$, $\gamma = 0.83$, the critical exponent $\delta = 1 + \gamma/\beta = 2.84$. The critical exponents determined for $Mn_{0.9}Ti_{0.1}CoGe$ - $\beta = 0.45$, $\delta = 2.84$ and $\gamma = 0.83$ - are similar to the theoretical values of the mean-field model for which β=0.5, δ=3.0 and γ=1.0, consistent with the existence of a long-range ferromagnetic interactions [27].

Figure 3(a) shows neutron diffraction patterns collected at T=3 K, 150 K, 200 K, 300 K and 350 K; these temperatures were selected in order to investigate the crystallographic and magnetic structures of $Mn_{0.9}Ti_{0.1}CoGe$ around the transition temperatures $T_{str} \sim 178$ K and $T_C \sim 280$ K. Refinements confirm that at 300 K and 350 K (i.e. above $T_C = 280$ K), the sample crystallizes in the hexagonal Ni_2In-type structure of P63/mmc space group and is in the paramagnetic state. By comparison at 200 K, while the crystal structure remains hexagonal, the enhanced magnetic scattering (e.g. the (100) and (110) Reflections) confirms that at 200 K $Mn_{0.9}Ti_{0.1}CoGe$ is ferromagnetic. Refinement of the 200 K pattern (Fig. 3(a)) leads to magnetic moment values of μ(Mn)=2.3 μ_B and μ(Co)=0.6 μ_B – total moment μ^{tot}= 2.9 μ_B for the hexagonal structure of $Mn_{0.9}Ti_{0.1}CoGe$ at 200 K, which is quite close to the value of M_s (2.3 μ_B) derived from magnetic measurement above.

As further indicated by the refinement of the diffraction pattern of Fig. 3(a) at 150 K, i.e. below T_{str} ~ 178 K, on decreasing the temperature below T_{str}, the structure changes from single phase hexagonal to co-existence of the hexagonal Ni_2In-type structure (P63/mmc) of phase fraction 54(2)% and the orthorhombic TiNiSi-type structure (space group Pnma) of phase fraction 46(2)%. Given the large number of fitted parameters introduced constraints during the refinements, we assume that the atomic magnetic moments of P63/mmc phase remain constant in the magnetic region. The resultant magnetic moments for the Pnma phase are $\mu(Mn)$=3.1 μ_B and $\mu(Co)$=0.9 μ_B at 150 K, thus indicating the orthorhombic structure has a higher magnetic moment than the hexagonal structure, as expected by *ab initio* total energy calculations [17, 26] and agreeing well with our magnetic measurements mentioned above (Fig. 1(b). This behaviour, with the moment in the orthorhombic phase larger than that in the hexagonal phase, is similar to that reported for the parent MnCoGe compound in which the value of the saturation moment for the orthorhombic structure is M_S^{orth} = 4:13 μ_B [16] while in the hexagonal structure, M_S^{hex} =2.76 μ_B [28]. Refinement of the neutron diffraction pattern at 3 K (Fig. 3(a)), shows the fraction of the hexagonal P63/mmc phase has decreased to 43(1)% with the orthorhombic Pnma phase increasing to 57(1)%. In the case of $Mn_{0.94}Ti_{0.06}CoGe$, however, it was found that below T_{str} (at ~235 K, [25]) the $Mn_{0.94}Ti_{0.06}CoGe$ phase exhibits 100% of the orthorhombic TiNiSi-type structure. So, it indicates again that the stability of hexagonal P63/mmc phase is enhanced due to the substitution of Ti for Mn.

Fig. 3(b) shows the temperature dependence of the lattice parameters and unit cell volumes together with the fractions of the hexagonal and orthorhombic phases of $Mn_{0.9}Ti_{0.1}CoGe$ as derived from refinements of the neutron data. In order to compare directly, we modify the lattice parameters of orthorhombic and hexagonal structures using the relationships $a_{ortho}=c_{hex}$, $b_{ortho}=a_{hex}$, $c_{ortho}=\_3a_{hex}$, and $V_{ortho}=2V_{hex}$ [15]. As is evident from Fig. 3(b), the

change in crystal structure from hexagonal P63/mmc to orthorhombic Pnma is associated with an increment in the unit cell volume of around ~4.04 percent. The change in unit cell volume, similar to that observed in $Mn_{1.07}Co_{0.92}Ge$ for which a change of $\Delta V/V$~5.3%, was obtained around T_{str} ~210 K [29].

The isothermal entropy change corresponding to magnetic field change ΔB (starting from zero field) can be conveniently derived from the magnetization data using the Maxwell relation [e.g. 2–6]:

$$\Delta S_M(T,B) = \int_0^B (\tfrac{\partial M(T,B)}{\partial T})_B dB \qquad (1).$$

Use of the Maxwell relation (Eqn. (1)) in determining ΔS_M from first order magnetic transition (FOMT) has been discussed thoroughly in the literature [e.g. 1, 3, 30-32]; this has led to deep insight to the suitability of different experimental and related analytical approaches in order to establish the isothermal entropy change. In the case of $Mn_{0.9}Ti_{0.1}CoGe$, the absence of field hysteresis in the magnetisation data around T_{str} (see Fig. 1(b)), indicates that this Maxwell method can be applied to determining the entropy change around T_{str}. The temperature dependence of the magnetic entropy changes in the region of T_{str} ~ 178 K and T_C ~ 280 K are shown in Fig. 4(a) with the curves for decreasing field and increasing field found to be essentially identical. Fig. 4(a) also reveals that the entropy change is significantly higher at T_{str} of maximum value $-\Delta S_M^{max}$ ~ 6.6 J/kg K, compared with the value at T_C of $-\Delta S_M^{max}$ ~ 4.2 J/kg K for a field change of ΔB=8 T. Fig. 4(b) shows the maximum values derived for the entropy change $-\Delta S_M^{max}$ around T_{str} and T_C as a function of magnetic field values, it can be seen clearly that with increasing field, the value of ΔS_M^{max} around T_{str} increases much faster than around T_C. As shown by the fit to the $-\Delta S_M^{max}$ values around T_C in Fig. 4(b), the data at the ferromagnetic transition can be well described by the functional form $-\Delta S_M^{max} \propto B^{2/3}$ [33]. This behaviour confirms the second-order character of

the phase transition around T_C as concluded from analysis of the Arrott plots of Fig. 1(c). On the other hand, it was found that in the region around the structural transformation at T_{str} ~ 178 K, the maximum values of the entropy change $-\Delta S_M^{max}$ vary linearly with magnetic field, indicating the existence of the proportional relationship $-\Delta S_M^{max} \propto B$ at this transition. It is well accepted that the total entropy can be written as sum of magnetic, lattice and electronic entropies. In general, all three contributions depend on temperature and magnetic field and cannot be clearly separated. Compared with the transition around T_C, , the total entropy for the phase transition around T_{str} should be expected coming from two major contributions: (1) magnetic part due to the magnetization drop (the Ms difference in orthorhombic structure and in the hexagonal structure); (2) lattice entropy change due to the crystal structure change from orthorhombic Pnma to hexagonal P63/mmc with a ~4.04 percent decrease in the unit cell volume, which is significant based on ref [34] where it was concluded that lattice entropy is proportional to the difference of phase volumes for the two phases involved in the first-order transformation.

Conclusions

The structural and magnetic properties of $Mn_{0.9}Ti_{0.1}CoGe$ compound have been investigated by magnetic (5 - 320 K; 0 – 8 T) and neutron diffraction (3 – 350 K) measurements. Substitution of Ti for Mn in the parent MnCoGe compound leads to a significant reduction in both T_{str} (from ~645 K for MnCoGe to ~178 K for $Mn_{0.9}Ti_{0.1}CoGe$) and T_C (from ~345 K for MnCoGe to ~280 K for $Mn_{0.9}Ti_{0.1}CoGe$). $Mn_{0.9}Ti_{0.1}CoGe$ exhibits a single phase with the hexagonal Ni_2In-type structure above T_{str} ~178 K while below T_{str} the hexagonal structure is found to co-exist with the orthorhombic TiNiSi-type structure, leading to phase fractions of 43(1)% and 58(1)% respectively at 3 K. The unit cell volume is found to expand around 4% on cooling below T_{str} ~178 K along with an increase in magnetic moment of around 31%.

The field dependence of the maximum of magnetic entropy change ΔS_M^{max} around T_C can be expressed as $\Delta S_M^{max} \propto B^{2/3}$ as expected for a second order magnetic transition while the relationship $\Delta S_M^{max} \propto B$ applies around the structural transition temperature T_{str}, which may be ascribed to the lattice entropy contribution.

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Figure captions

Fig. 1 (a) Temperature dependence of the magnetization of $Mn_{0.9}Ti_{0.1}CoGe$ as measured in the magnetic fields indicated (B=0.01 T, 0.1 T and 4 T). The inset of Fig. 1(a) shows the expanded temperature range for B=0.01 T; the transition temperatures T_{str} and T_C are marked by arrows; (b) Temperature dependence of magnetization for $Mn_{0.9}Ti_{0.1}CoGe$ (B = 0-8 T) as measured at various temperatures around T_{str} and T_C, and (c) the corresponding Arrott plots of M^2 vs B/M as determined from the data of Fig. 1(b).

Fig. 2 (a) Spontaneous magnetization values M_s for $Mn_{0.9}Ti_{0.1}CoGe$ as a function of temperature as derived from Figs. 1(b) and 1(c). (b) Kouvel-Fisher plots of $M_s(T)(dM_s/dT)^{-1}$ (*left scale*) and $\chi_0^{-1}(T)(d\chi_0/dT)^{-1}$ (*right scale*) versus temperature. The lines are fits to the data around T_C as discussed in the text with fits leading to the critical exponent values $\beta = 0.45$, $\gamma = 0.83$, and hence $\delta = 1 + \gamma/\beta = 2.84$.

Fig. 3 (a) Neutron diffraction patterns of $Mn_{0.9}Ti_{0.1}CoGe$ at T=3 K, 150 K, 200 K, 300 K and 350 K ($\lambda = 1.622$ Å). The full lines through the data represent Rietveld refinements to the hexagonal Ni_2In-type structure (P63/mmc; upper set of markers) and the orthorhombic TiNiSi-type structure (space group Pnma; lower set of markers) as discussed in the text. (b) The unit cell volumes and lattice parameters together with the fractions of the hexagonal and orthorhombic phases of $Mn_{0.9}Ti_{0.1}CoGe$ as a function of temperature.
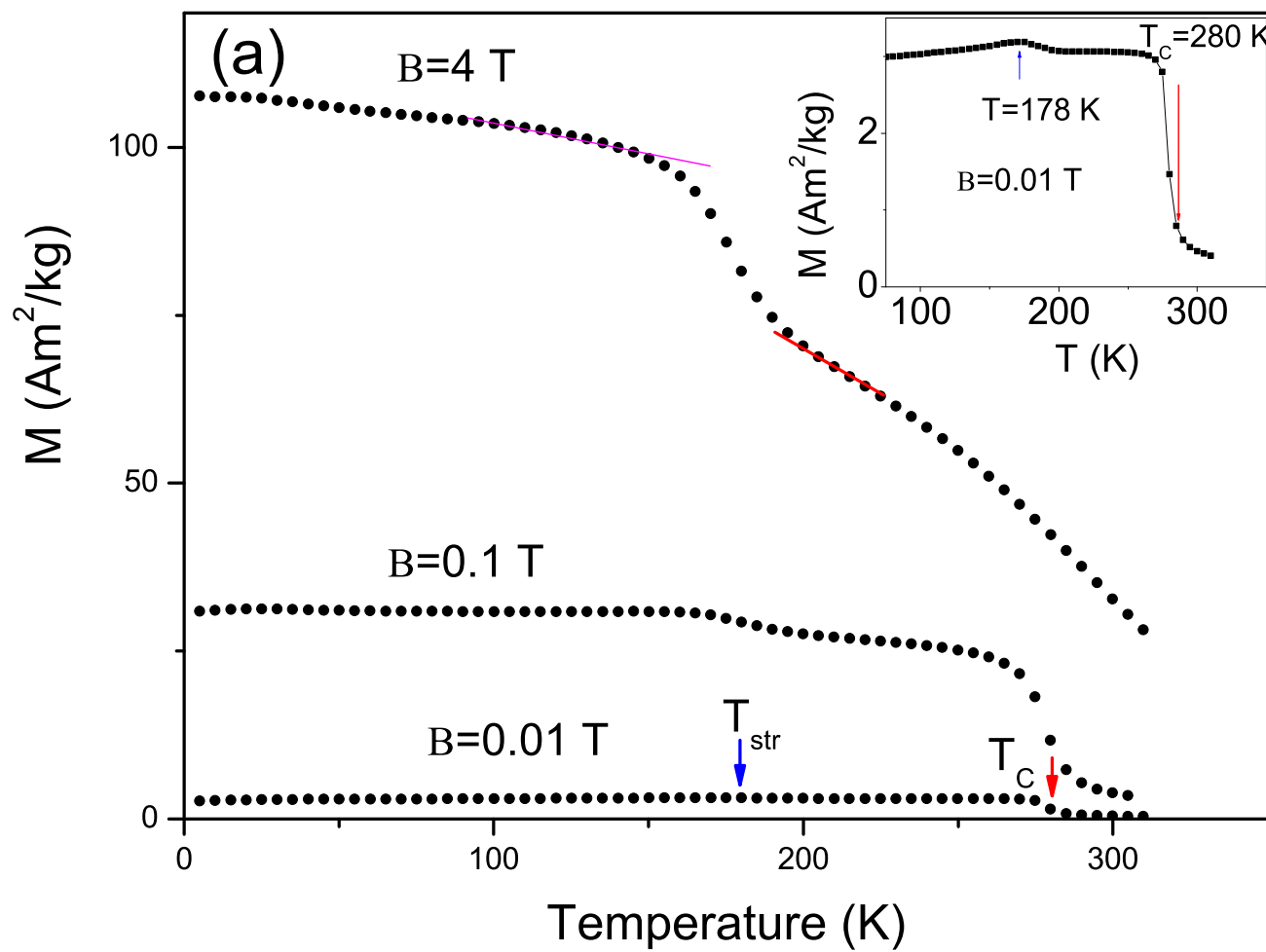
Fig. 4 (a) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M(T, B)$ as calculated from the magnetization isotherms; (b) Graphs of the maximum values of the magnetic entropy change $-\Delta S_M^{max}$ in the region of $T_{str} \sim 178$ K and $T_C \sim 280$ K as

functions of magnetic field B. The dashed lines represent fits to these data as discussed in the text.

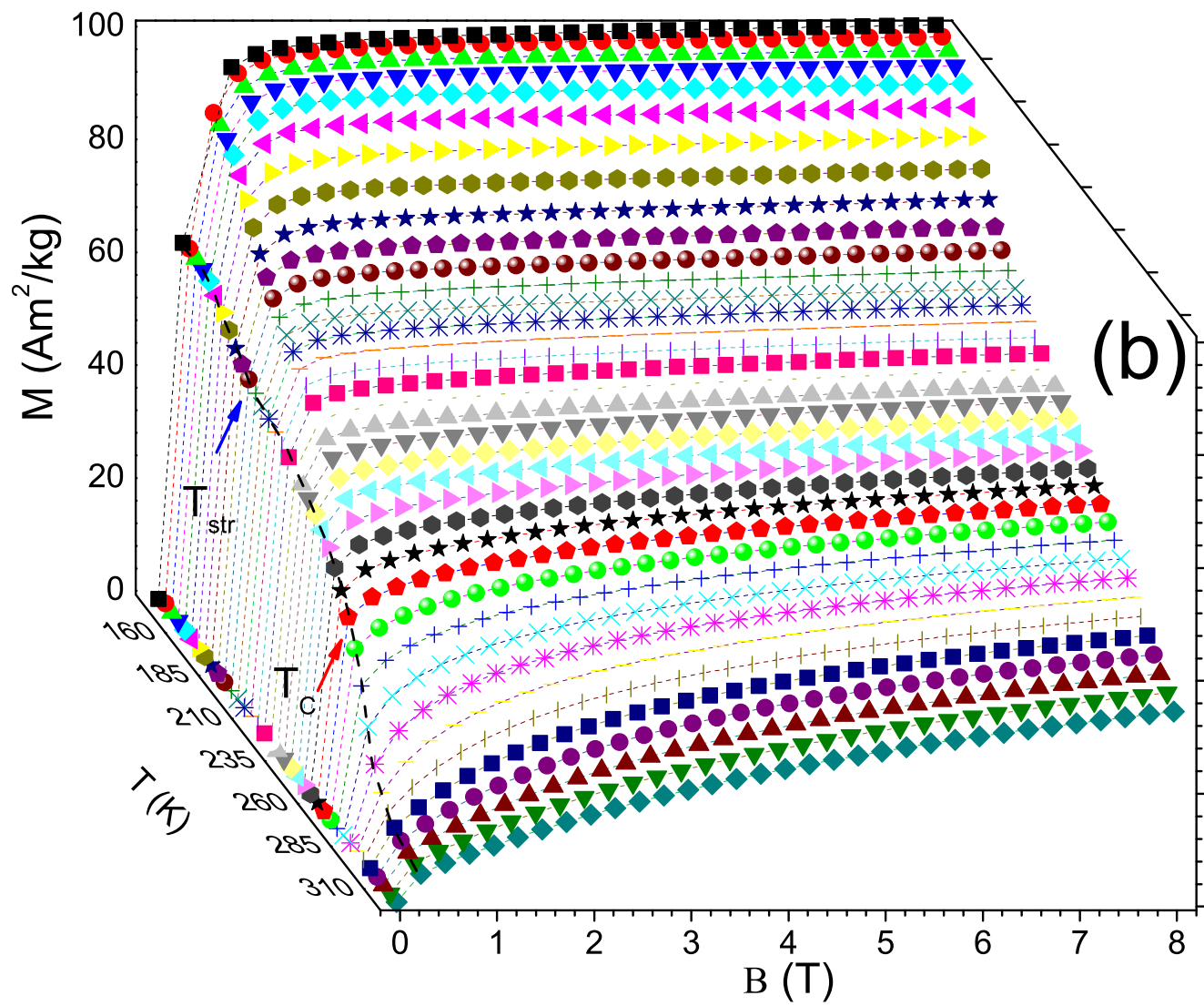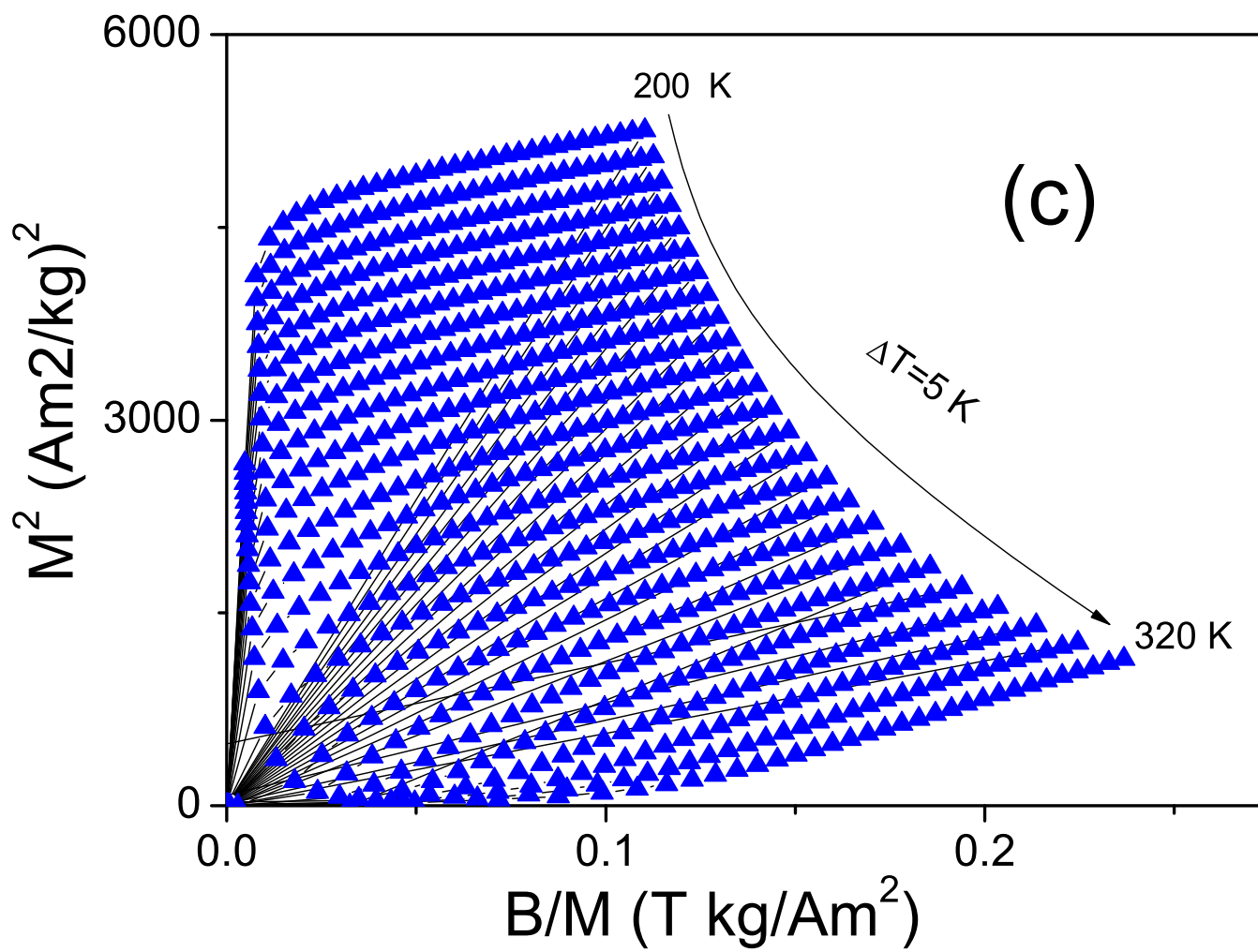- We detected and confirmed two magnetic phase transitions at ~178 K and ~280 K

- Both structural entropy and magnetic entropy contribute to the entropy change around T_{str}.

- $-\Delta S_M^{max}$ can be expressed as $-\Delta S_M^{max} \propto B^n$ with n=1 around T_{str} and n=2/3 around T_C.

(c)