Magnetostructural phase transitions and magnetocaloric effects in as-cast $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ compounds

Anil Aryal^{a,*}, Abdiel Quetz^a, Sudip Pandey^a, Tapas Samanta^c, Igor Dubenko^a, Margaret Hill^b,
Dipanjan Mazumdar^a, Shane Stadler^c, and Naushad Ali^a

Abstract:

The structural and magnetic properties of as-cast $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ ($0 \leq x \leq 0.05$) have been studied by X-ray diffraction, differential scanning calorimetry, and magnetization measurements. The partial substitution of Al for Mn in $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ results in a decrease in the martensitic transition temperature T_M . For the concentration range $0 \leq x \leq 0.01$, T_M was found to coincide with ferromagnetic transition temperature (T_C) resulting in a first-order magnetostructural transition (MST). A further increase in aluminum concentration resulted in a splitting of the phase transition temperatures, which included a drastic decrease in the martensitic temperature. The compounds with $x > 0.02$ showed a single transition at T_C . The maximum values of the magnetic entropy changes ($-\Delta S_M$) were ~ 18 J/kgK, 12 J/kgK, and 7 J/kgK for $\Delta H = 5$ T at 313 K ($x = 0.00$), 286 K ($x = 0.01$), and 220 K ($x = 0.02$), respectively. The maximum value of the relative cooling power (RCP) was found to be 303 J/kg for $x = 0.01$ at $T = 286$ K for $\Delta H = 5$ T. It

has been established that as-cast samples of this system show large value of MCE near room temperature making this system a promising material for magnetic cooling technologies.

1. Introduction

The magnetocaloric effect (MCE) refers to an adiabatic temperature change (ΔT_A) or isothermal magnetic entropy change (ΔS_M) in a magnetic material, induced by an applied magnetic field. Near room temperature MCE has been a subject of interest for decades because of its potential application in magnetic refrigeration, which is a possible eco-friendly and energy efficient cooling technology alternative to the conventional vapor cycle refrigeration [1, 2]. The largest MCEs have been observed in several materials such as $Gd_5Si_2Ge_2$ [3], $MnFe(P,As)$ [4], $LaFe_{13-x}Si_x$ [5], $NiMn(Ga,Sb,In)$ based Heusler alloys [6], and $MnAs_{1-x}Sb_x$ [7], which show first-order simultaneous transitions in the magnetic and crystal structures, i.e., magnetostructural transitions (MSTs). The mechanisms responsible for the MSTs are not completely understood, and hence the exploration and study of the new materials that exhibit MSTs is important for applications and fundamental physics.

$MnCoGe$ belongs to a wider class of materials with composition $MM'X$, where M, M' are 3d transition metals and X is Si or Ge. Stoichiometric $MnCoGe$ has a ferromagnetic (FM) phase below the Curie temperature ($T_C \sim 345$ K). It transforms to a high-temperature, hexagonal Ni_2In -type structure from a low-temperature orthorhombic $TiNiSi$ -type structure at $T_M \sim 650$ K in the paramagnetic (PM) region [8]. If the structural transition temperature (T_M) is tuned to coincide with T_C , a magnetostructural phase transition (MST) with large change in magnetization can be expected, which enhances the potential for large MCE. It has been reported that changes in stoichiometry, chemical composition, or application of external pressure can result in the

coincidence of the magnetic and structural transitions, therefore may increase the magnetic entropy change to show a large MCE [9-16]. The effects of substituting Al for Co or Ge in MnCoGe have been reported in Refs. [17, 18]. Recently, Si, et. al. [19] showed the parent MnCoGe compound is in the hexagonal phase at room temperature and the crystal structure changes to orthorhombic by substituting Al in Mn sites. Various groups working in this system previously have reported different T_M values ranging from 420 K to 650 K [8, 9, 15, 20]. The reason behind such variation in the martensitic temperature is identified as a change in crystallographic order due to composition and heat treatment methods [21]. This seems to indicate that the MnCoGe system is sensitive to the sample synthesis procedure and heat treatment. In this work, we present the results of our study on the partial substitution of Al for Mn in the $Mn_{1-x}Al_xCoGe$ system, which exhibits a MST and leads to a large MCE near room temperature.

2. Experimental Details

Polycrystalline $Mn_{1-x}Al_xCoGe$ samples with nominal compositions $0 \leq x \leq 0.05$ were synthesized by arc-melting high purity elements (99.99%) in an ultra-high purity argon atmosphere. The samples were turned over and re-melted 4 times to ensure better homogeneity. Mass loss after melting was found to be between 0.03-0.3% for the compounds with $0.00 < x \leq 0.05$. For $x = 0.00$, a 0.7% loss in mass was recorded. Assuming mass loss in Mn only, the samples can be considered slightly off-stoichiometric. As-cast samples were used for all measurements. The crystal structure was studied by powder X-ray diffraction (XRD) using $CuK\alpha$ radiation at room temperature. The XRD pattern has been indexed for hexagonal and orthorhombic phases. The cell parameters of high temperature (hexagonal phase) have been

calculated using the refined curves. The magnetic properties of the $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ compounds were measured using a SQUID magnetometer (Quantum Design) in the temperature interval 5 - 380 K in applied magnetic fields up to 5 T. Magnetic measurements were taken following zero field cooled (ZFC) and field cooled (FC)-protocols. Differential scanning calorimetry (DSC) measurements were obtained using a DSC 8000 instrument (with a ramp rate of 30 K/min during heating and cooling) in the temperature range 123 - 423 K. Latent heat (L) was estimated from the endothermic peaks of the heat flow curves using $L = \int_{T_s}^{T_f} \frac{dQ}{dT} dT$, where $\frac{dQ}{dT}$ is the change in heat flow with respect to temperature, and T_s and T_f are initial and final temperatures of the magnetostructural phase transition on heating.

3. Results and Discussion

The room temperature XRD patterns for the as-cast $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ compounds are shown in Fig. 1(a). For $x = 0$, the orthorhombic (TiNiSi-type) and hexagonal (Ni_2In -type) phases coexist indicating that the structural transition in this compound occurs near room temperature. At lower Al concentration, $x = 0.01$, the hexagonal (Ni_2In -type) structure stabilizes near room temperature with a small trace of orthorhombic phase. With a further increase in Al concentration ($x = 0.02, 0.03, 0.05$), the compounds crystallize in a single-phase hexagonal Ni_2In -type structure. This indicates that the partial substitution of Al for Mn in $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ serves to stabilize the high temperature austenite phase. The above results from XRD are in accordance with the results presented in earlier studies for similar systems [17, 18, 22, and 23] and contrast with results presented in [19].

The Rietveld refinements of the XRD patterns (hexagonal phase) of the representative compounds ($x = 0.01$ and 0.02) are shown in Fig. 1(b) and (c). The calculated values of the

lattice parameters and corresponding unit cell volumes for various Al concentrations are shown in Table 1. It is interesting to note that the cell parameters of the $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ compound follow Vegard's law [24] for small Al concentrations. The volumes of the crystal cells and cell parameters were found to increase in the interval $x = 0.00 - 0.02$, and decrease with larger aluminium concentrations. The increase in the cell parameters was expected due to the larger metallic radius of Al (1.432 Å) compared to Mn (1.264 Å) [25]. The decrease in crystal cell volume when the Al concentration $x > 0.02$ is most likely related to the increase in the thermal expansion coefficient with aluminum content. However detailed temperature-dependent XRD studies are required to make strong conclusions concerning the reason of such anomalous behavior.

Fig. 2(a) shows the temperature dependence of the magnetization $M(T)$ of the as-cast $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ compounds with $0 \leq x \leq 0.05$. The $M(T)$ curves were measured during heating and cooling cycles from 10 K – 380 K in an applied magnetic field of 100 Oe. All of the compounds show ferromagnetic order at low temperatures. On increasing temperature, a large drop in magnetization typical for a FM to PM transition at T_C was observed. Compounds with $x = 0.00, 0.01$, and 0.02 show a thermal hysteresis of 10 K, 7 K, and 7 K, respectively, between heating and cooling cycles. The thermal hysteresis in magnetization is a signature of the temperature induced first-order transition, and therefore indicates a first-order structural transformation in these compounds at T_M . For the compounds with $x = 0.00$ and $x = 0.01$, the magnetic transition temperature (T_C) and the structural transition temperature (T_M) coincide to produce a first-order MST from a FM TiNiSi – type phase to a PM Ni_2In - type phase. It has been reported earlier that stoichiometric MnCoGe has $T_C \sim 345 \text{ K} < T_M \sim 650 \text{ K}$ and its magnetic

properties are extremely sensitive to Mn concentration. Any deviation from stoichiometry shifts T_M to a lower temperature so that it may coincide with T_C to form a MST [15, 16].

The 0.7% loss in mass for the compound with $x = 0.00$ (assuming only Mn loss) corresponds to the molar composition $Mn_{0.98}CoGe$. Hence, for $x = 0.00$, the observed MST near room temperature can be explained as a result of a small deviation from stoichiometry that lowers T_M to coincide with T_C . The observed hexagonal Ni_2In -type phase in the XRD pattern at room temperature also supports the above argument. For $x = 0.02$, T_M falls below T_C , and the magnetic and structural transitions decouple. The temperature induced structural transition vanishes in compounds with $x = 0.03$ and 0.05 . Only a second order magnetic transition (SOT) from a FM to PM state was observed in these compounds. The values of the transition temperatures calculated from the minimum of dM/dT in the magnetization curve during the heating cycle are listed in Table 2. Thus, by partial substitution of Al for Mn in $MnCoGe$, T_M linearly decreased from 313 K to 220 K and a first-order MST was observed when T_M and T_C coincided near room temperature. The first-order MST seen in the $M(T)$ curves for $x = 0.00$, 0.01 , and 0.02 were further confirmed by DSC measurements (see Fig 2(b)). The values of the transition temperatures, latent heat (L), thermal hysteresis, and total entropy change ($-\Delta S_T$) are given in Table 2.

The field dependence of magnetization $M(H)$ at $T = 5$ K is shown in inset of Fig 2(a). The $M(H)$ curves indicate that all of the compounds possess ferromagnetic ordering in the ground state. The saturation magnetization decreases linearly with increasing Al concentration with a large drop for $x = 0.03$ and $x = 0.05$. Hence, it can be concluded that for compounds that undergo a temperature induced structural transition, the structural change has a significant contribution to the increase in the magnetization in the ground state.

The magnetic entropy change ($-\Delta S_M$) near the transition temperature for field changes up to 5 T are plotted in Fig. 4. The $-\Delta S_M$ values were calculated from the isothermal magnetization curves $M(H)$ (shown in Fig. 3) using Maxwell's relation, $\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH$ [1, 2]. The Maxwell's relation cannot be used to evaluate ΔS_M for ideal FOTs. Ideally, the transition is perfectly discontinuous i.e. $\left(\frac{\partial M}{\partial T} \right)_H$ does not exist at the transition temperature. However, most materials do not show ideal discontinuities at the FOT. The changes in $\left(\frac{\partial M}{\partial T} \right)_H$ are finite and can be calculated experimentally. Therefore, the Maxwell relation can be used to estimate ΔS_M at a FOT in these cases [28]. Relatively large magnetic entropy values of $-\Delta S_M = 18$ J/kgK (at $T = 313$ K, $\Delta H = 5$ T) and 12 J/kgK (at $T = 286$ K, $\Delta H = 5$ T) were obtained for $x = 0.00$ and 0.01, respectively. For $x = 0.02$, the $-\Delta S_M$ values corresponding to a first-order structural transition and a SOT were found to be 7 and 3 J/kgK, respectively. The $-\Delta S_M$ values of the compounds with higher Al content ($x = 0.03$ and $x = 0.05$) near the SOT were 3.5 and 3.2 J/kgK, respectively. The above results show that, by a partial substitution of Mn by Al, the magnetic and structure transition temperatures can be tuned to coincide, resulting in an increase in the magnetization and, finally, resulting in a large $-\Delta S_M$. The observed values of $-\Delta S_M$ are larger than or comparable with other well-known giant MCE materials such as $\text{Gd}_5\text{Si}_2\text{Ge}_2$, $\text{MnCoGeB}_{0.01}$, $\text{Mn}_{1-x}\text{Cr}_x\text{CoGe}$ (with $x = 0.18$ and 0.25), $\text{MnFeP}_{0.45}\text{As}_{0.55}$ and $\text{La}_{0.70}\text{Ca}_{0.30-x}\text{Sr}_x\text{MnO}_3:\text{Ag}_{0.10}$ manganites [3, 4, 10, 11, 26]. The values of $-\Delta S_M$ obtained are larger than those of the $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ (heat treated and quenched samples, $\Delta H = 5$ T) [19] which shows a better enhancement of magnetocaloric properties in this system.

The relative cooling power (RCP) is an important parameter that estimates the usefulness of a material as a magnetic refrigerant, and can be used to compare different materials. The RCP is a measure of amount of heat transferred between the hot and cold reservoirs in an ideal refrigeration cycle and is defined as: $RCP = -\Delta S_M (\text{max}) \times \Delta T_{FWHM}$, where ΔT_{FWHM} is the full-width-at-half-maximum of the $-\Delta S_M$ curve [27]. Large values of the RCP = 250 and 303 J/kg with $\Delta H = 5T$ were found for the compounds with $x = 0.00$ and 0.01 (those show a MST). For $x = 0.03$, RCP = 252 J/kg. The experimental results are summarized in Table 2.

A concentration dependent phase diagram has been constructed (Fig.5) using the DSC and magnetization data (Table 2). Substituting Al for Mn leads to a linear decrease in T_M from 313 K to 220 K. For the concentration range $0 \leq x \leq 0.01$, T_M coincides with T_C to form a first-order MST from a FM orthorhombic (TiNiSi-type) structure to a PM hexagonal (Ni₂In-type) structure close to room temperature. For $0.01 < x \leq 0.02$, T_M is below T_C , and the magnetic and structural transitions decouple. These compounds undergo structural transitions from an orthorhombic (TiNiSi-type) to hexagonal (Ni₂In-type) structure in the FM state, followed by a magnetic transition from FM to PM state with hexagonal structure. The compounds with $x > 0.02$ stabilize in a hexagonal (Ni₂In-type) structure without a detectable martensitic transformation below T_C , and undergo magnetic transitions from a FM to a PM state.

4. Conclusions

The magnetostructural phase transitions and magnetic entropy changes in as-cast Mn_{1-x}Al_xCoGe compounds have been studied. Through the partial substitution of Al for Mn the martensitic transformation temperature decreased and, as a result, a first-order MST formed for $0 \leq x \leq 0.01$. For $0.01 < x \leq 0.02$, T_M is below T_C and the magnetic and structure transitions

separate. Compounds with $x > 0.02$ form a Ni_2In -type austenite phase with no distinct martensitic transformation below T_C . Large values of $-\Delta S_M$ and RCP corresponding to first-order MSTs and SOTs were observed near room temperature. Thus, large values of the magnetic entropy change, RCP, small thermal hysteresis, and non-toxic and less-expensive constituent elements makes this system a promising material for room-temperature magnetic cooling technologies.

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References:

- [1] K. A. Gschneidner Jr, V. K. Pecharsky, and A. O. Tsokol Rep. Prog. Phys. **68**, 1479 (2005)
- [2] A. M. Tishin and Y. I. Spichkin, The Magnetocaloric Effect and its Applications Great Britain Institute of Physics (2003)
- [3] V. K. Pecharsky and K. A. Gschneidner Jr., Phys. Rev. Lett. **78**, 4494 (1997)
- [4] O. Tegus, E. Bruck, K. H. J. Buschow and F. R. de Boer, Nature **415**, 150 (2002)
- [5] A. Fujita, S. Fujieda, Y. Hasegawa and K. Fukamichi, Phys. Rev. B **67**, 104416 (2003)
- [6] I. Dubenko, M. Khan, A. K. Pathak, B. R. Gautam, S. Stadler and N. Ali, J. Magn. Magn. Mater. **321**, 754 (2009)
- [7] H. Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001)
- [8] T. Kanomata, H. Ishigaki, T. Suzuki, H. Yoshida, S. Abe, T. Kaneko, J. Magn. Magn. Mater., **131**, 140 (1995)

- [9] J. T. Wang, D. S. Wang, C. Chen, O. Nashima, T. Kanomata, H. Mizuseki, and Y. Kawazoe, Appl. Phys. Lett. **89**, 262504 (2006)
- [10] N. T. Trung, L. Zhang, L. Caron, K. H. J. Buschow, and E. Bruck, Appl. Phys. Lett. **96**, 172504 (2010)
- [11] N. T. Trung, V. Biharie, L. Zhang, L. Caron, K. H. J. Buschow and E. Bruck, Appl. Phys. Lett. **96**, 162507 (2010)
- [12] E. K. Liu, W. Zhu, L. Feng, J. L. Chen, W. H. Wang, G. H. Wu, H. Y. Liu, F. B. Meng, H. Z. Luo, Y. X. Li , Europhys. Lett. **91**, 17003 (2010)
- [13] L. Caron, N. T. Trung and E. Bruck, Phys. Rev. B **84**, 020414(R) (2011)
- [14] S. Niziol, R. Zach, J. P. Senateur and J. Beille, J. Magn. Magn. Mater. **79**, 333 (1989)
- [15] V. Johnson, Inorg. Chem. **14**, 1117 (1975)
- [16] P. E. Markin, N. V. Mushnikov, V. I. Khrabrov and M. A. Korotin, The Physics of metals and metallography, **106**, 5 (2008)
- [17] W. Zhang, O. Tegus, Y. Wu, Yirgeltu, H. Yan and S. Lin, J. Mater. Sci. Technol. **25**, 781 (2009)
- [18] L. F. Bao, F. X. Hu, R. R. Wu, J. Wang, L. Chen, J. R. Sun, B. G. Shen, L. Li, B. Zhang and X. X. Zhang, J. Phys. D: Appl. Phys. **47**, 055003 (2014)
- [19] X. Si, Y. Liu, X. Lu, W. Wang, W. Lei, J. Lin, T. Zhou, and Y. Xu, Journal of Applied Physics **119**, 215104 (2016)
- [20] K. Koyama, M. Sakai, T. Kanomata, and K. Watanabe, Jpn. J. Appl. Phys., Part 1 **43**, 8036 (2004)
- [21] S. Yuce, N. M. Bruno, B. Emre, and I. Karaman, Journal of Applied Physics **119**, 133901 (2016)

- [22] T. Samanta, I. Dubenko, A. Quetz, S. Stadler, and N. Ali, Journal of Applied Physics **113**, 17A922 (2013)
- [23] T. Samanta, I. Dubenko, A. Quetz, S. Stadler, and N. Ali, Applied Physics Letters **101**, 242405 (2012)
- [24] L. Vegard, Z. Phys., **5** 17 (1921)
- [25] W. B. Pearson, The Crystal Chemistry and Physics of Metals and Alloys New York Wiley-interscience (1972)
- [26] R. Jha, S. K. Singh, A. Kumar, V. P. S. Awana, J. Magn. Magn. Mater. **324**, 2849 (2012)
- [27] A. Aryal, A. Quetz, S. Pandey, T. Samanta, I. Dubenko, D. Mazumdar, S. Stadler and N. Ali, J. Appl. Phys. **119**, 043905 (2016)
- [28] K. A. Gschneidner, Jr. and V .K. Pecharsky “Magnetocaloric materials,” Ann. Rev. Mater. Sci., **30**, 387 (2000).

List of Tables

Table 1: Lattice parameters and unit cell volumes of hexagonal phase of $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ at room temperature.

Concentration (x)	a (Å)	c (Å)	Volume (Å ³)
0.00	4.089(1)	5.312(2)	76.91(6)
0.01	4.094(1)	5.325(1)	77.32(3)
0.02	4.0954(6)	5.3268(9)	77.37(2)
0.03	4.0860(5)	5.3146(7)	76.84(1)
0.05	4.0774(5)	5.2981(7)	76.28(1)

Table 2: Type of phase transition, values of phase transition temperatures, maximum entropy change, RCP, L, and thermal hysteresis $(\Delta T)_{\text{hyst}}$ obtained from magnetization and DSC measurements for $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ compounds. All of the values tabulated below correspond to the heating cycles.

x	Type of phase transition	Magnetization measurement					DSC measurement			
		T_C (K)	T_M (K)	$-\Delta S_M$ (J/kg K) $\Delta H = 5T$	RCP (J/Kg) $\Delta H = 5T$	$(\Delta T)_{\text{hyst}}$ (K)	T_M (K)	L (J/g)	$-\Delta S_T$ (J/kg K)	$(\Delta T)_{\text{hyst}}$ (K)
0.00*	FM-PM	345	650							
0.00	MST FM-PM	313	313	18	250	10	313	7.74	25	16
0.01	MST FM-PM	286	286	12	303	7	297	10.63	36	17
0.02	structurally driven FOT	281	220	7 (T_M)	182 (T_M)	7	214	1.73	8	21
				3 (T_C)	217 (T_C)					
0.03	SOT FM-PM	281		3.5	252					
0.05	SOT FM-PM	281		3.2	259					

* Ref. [8]

Figure Captions:

Figure 1. a) Room temperature XRD patterns of $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ compounds with $0 \leq x \leq 0.05$. For $x = 0$, the orthorhombic peaks are indexed. For $x > 0$, the hexagonal peaks are indexed. The peaks with symbol “ β ” are from the K_β wavelength. (b), and (c) show the Rietveld refinements of the XRD patterns of the compounds with $x = 0.01$ and $x = 0.02$ for hexagonal phase.

Figure 2. a) The temperature dependence of the magnetization $M(T)$ for $\text{Mn}_{1-x}\text{Al}_x\text{CoGe}$ with $0 \leq x \leq 0.05$ on heating and cooling in an applied field of 100 Oe. The solid and open symbols represent heating and cooling cycles, respectively. Inset: Field dependence of the magnetization

M(H) at $T = 5$ K. b) DSC heat flow curves as a function of temperature. The arrows indicate the heating and cooling cycles.

Figure 3. Isothermal magnetization $M(H)$ curves for $Mn_{1-x}Al_xCoGe$ compounds with $x=0.00$ and 0.01 .

Figure 4. Magnetic entropy changes ($-\Delta S_M$) as a function of temperature for $Mn_{1-x}Al_xCoGe$ compounds with a magnetic field change $\Delta H = 5T$.

Figure 5. Concentration dependent phase diagram of $Mn_{1-x}Al_xCoGe$.

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