

Magnetic Properties and Magnetocaloric Effect of MnCoAl Compound

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ABSTRACT

This work investigates the substitution of main-group element Al for Ge in the MnCoGe system to study the effect of magnetic phase transition and the magnetocaloric effect of the compounds. The Room temperature X-ray diffraction indicates clearly that most of the reflections can be identified with the orthorhombic structure (TiNiSi-type, space group Pnma) for MnCoGe and the hexagonal structure (Ni₂In-type, space group P63/mmc) for MnCoAl. The substitution of Al for Ge in MnCoAl transmutes the crystal structure from TiNiSi-type to Ni₂In-type structure. The magnetic measurement revealed the curie temperatures, T_c decreases from 340 K to 285 K with the substitution of Al with Ge. Besides, the Arrott plots (M^2 against B/M) for the MnCoGe and MnCoAl, demonstrated characteristics of second-order transition for both samples. The calculated magnetic entropy change, $-\Delta S_M$ values shows no difference for increasing and decreasing fields, which confirms that there is no hysteresis loss occurred near the magnetic transition. The $-\Delta S_M$ maximal values is about $4.41 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for MnCoGe and $3.73 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ for MnCoAl, for a field change of 0-5 T.

Keywords: Magnetocaloric effect, Magnetocaloric materials, MnCoGe, Magnetic refrigeration, Magnetic entropy change

1. INTRODUCTION

Magnetic cooling was first suggested almost a century ago. Since then, the application of the magnetocaloric effect was largely in cooling to very low temperatures using paramagnetic salts for fundamental research. In more recent times, a wider range of materials has been considered with wider application in mind [1,2]. The magnetocaloric effect (MCE) is a fundamental magneto-thermal phenomenon known as the cooling or warming of a magnetic material in adiabatic conditions due to a change in applied magnetic field [3]. Figure 1 shows the illustration of the schematic representing the magnetic refrigeration cycle. As previously mentioned, the magnetocaloric effect is caused by entropy changes in magnetic materials caused by applying a magnetic field. The coupling between the two structures transfers energy between the lattice and magnetic entropies.

A great many material families with second-order magnetic phase transitions have been studied for the application of magnetocaloric effects, such as rare earth and related alloys (*e.g.* [4,5]), RT_2 Laves phases (R= rare earth, T= transition metal) (*e.g.* [6-8]), rare-earth manganites (*e.g.* [9,10]) and RT_2X_2 compounds (R= rare earth, T= transition metal, X= Si or Ge) (*e.g.* [11-13]).

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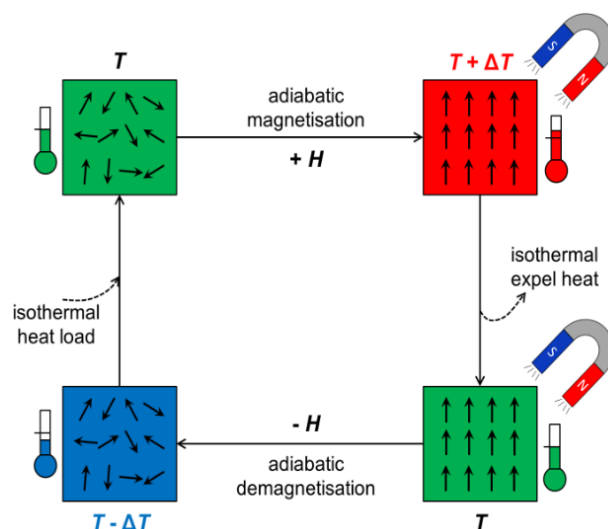


Figure 1. Schematic representation of a magnetic-refrigeration cycle

This work investigates the substitution of main-group element Al for Ge in the MnCoGe system. Previous research has revealed that magnetic moments are solely connected to Mn and Co atoms [14]. The replacement of Ge atoms with Al atoms can have an effect on transition temperatures and the surrounding environment [15]. The experiment found that the Al substitution stabilizes the Ni₂In-type structure (hexagonal, space group *P63/mmc*). As a result, the structural transition temperature (T_{str}) of MnCoAl is equal to the Curie temperature (T_c) value ~ 285 K which expected a large MCE as the overlap of magnetic and structural transitions.

2. MATERIAL AND METHODS

The MnCoAl compound was prepared by arc melting with appropriate amounts of Mn (99.9%), Co (99.9%) and Al (99.9%) chips in an argon atmosphere. The starting materials contained $\sim 3\%$ of Mn over the stoichiometric amount due to evaporation to compensate for the weight loss of Mn during melting. To achieve good homogeneity, the ingots were melted five times before wrapped in tantalum foil, sealed in an evacuated quartz tube and subsequently annealed at 900 °C for 120 hours. The samples were measured by using X-ray diffraction (XRD) (Cu K α radiation, $\lambda = 1.5418$ Å) and differential scanning calorimetry (DSC) measurements at room temperature. The magnetization measurements were performed in the temperature range of 10–600 K at applied fields of up to 55 T using the vibrating sample magnetometer option of a Quantum Design 14 T physical properties measurement system (PPMS).

3. RESULTS AND DISCUSSION

3.1 Structure Properties

Figure 2 shows the X-ray diffraction (XRD) patterns of MnCoGe and MnCoAl at room temperature. For MnCoAl, the peaks have been identified with the hexagonal phase Ni₂In-type structure (space group *P63/mmc*). In contrast, [3] reported the MnCoGe peak as orthorhombic phase also known as TiNiSi-type structure (space group *Pnma*) as depicted in the figure. These findings show that the crystal structure inhabit a change from TiNiSi-type structures to Ni₂In-type structures with the replacement of Al for Ge atoms, indicating that the martensitic transition temperatures of the two-alloy series drop from higher to lower temperatures. It was reported previously by MnCoGe_{1-x}Al_x, as the Al content increases, the pattern indexed to a mixed ratio of orthorhombic and hexagonal phases to a single hexagonal Ni₂In-type structure.

Alternatively, the substitution of Al for Ge tends to persist Ni₂In-type austenite and lower the T_{str} [15].

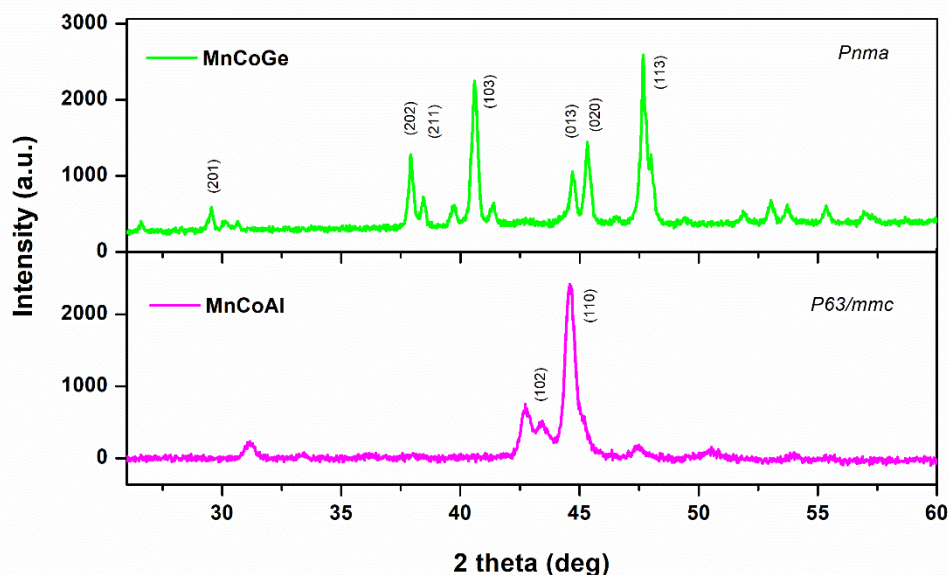


Figure 2. Powder XRD patterns of MnCoGe and MnCoAl measured at room temperature. The Miller indices hkl represent the typical Ni₂In-type hexagonal (bottom) and TiNiSi-type orthorhombic (top) structures.

3.2 Magnetic Phase Transitions

To determine the transition temperature, temperature-dependent magnetization (M–T curves) under a low field of 0.01 T and differential scanning calorimetry (DSC) measurements of MnCoAl and MnCoGe compounds were conducted ranging from 10–600 K, as depicted in Figure 3. For MnCoGe and MnCoAl, it was found that the T_c decreases (340 K – 285 K) with the substitution of Al with Ge. It can be observed with the sharp magnetic transition from the ferromagnetic phase, transit to the paramagnetic phase of MnCoGe shown in the figure. The same pattern shows in the previous report on MnCoGe_{1-x}Al_x [15], where the curie temperature decreases as Al content is increased (352 K to 269 K).

T_{str} is defined with the most significant slope that occurs in the measurement [15]. The DSC measurement indicated that the T_{str} of MnCoGe is higher than the T_c with $T_{str} = 450$ K. However, dM/dT plot as shown in inset Figure 3 a) indicated that the T_{str} of MnCoAl is equal to the T_c value ~ 285 K. A large MCE can be expected as the overlap of magnetic and structural transitions of MnCoAl. It is observed that the T_{str} is decreasing with the replacement of Ge by Al, hence will cause temperature change when cooled to low temperature.

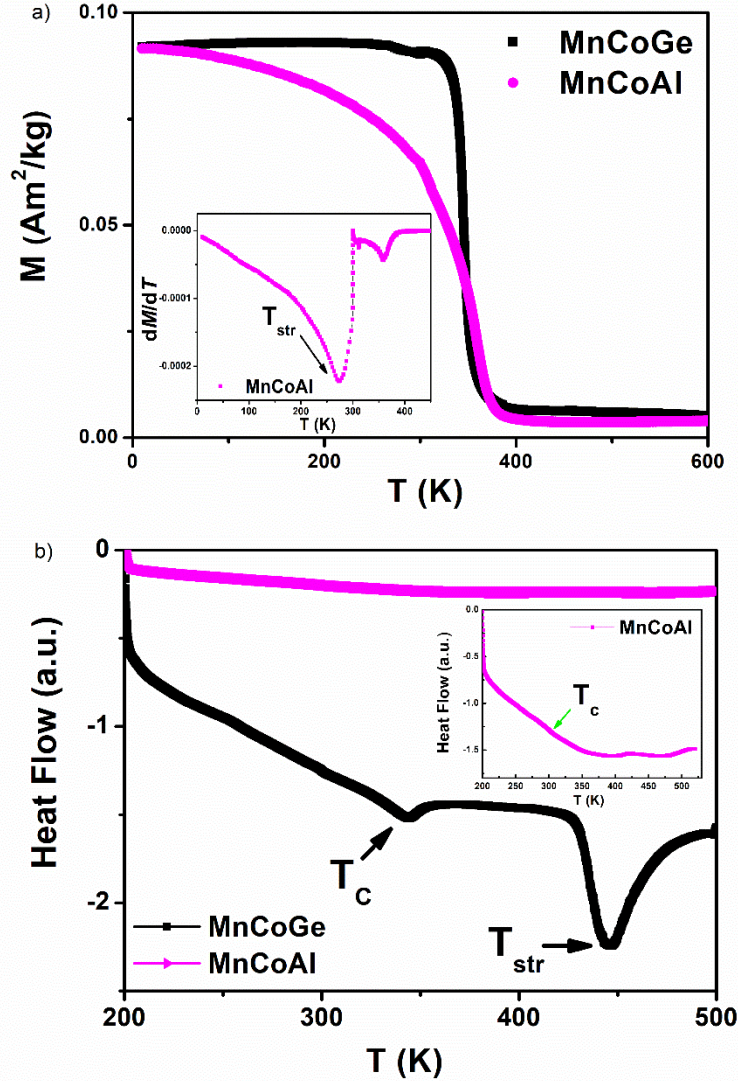


Figure 3. (a) M–T curves measured for MnCoGe and MnCoAl. The inset shows the pattern of dM/dT plot indicating the structural transition temperature, T_{str} . (b) DSC curves measured ranging from 300 to 500 K. The arrows indicate the Curie temperature, T_c and structural transition temperature, T_{str} .

3.3 The magnetocaloric effect

Figure 4 a) and b) illustrate the magnetization curves obtained for MnCoGe and MnCoAl for fields ranging from $B = 0$ –5 T from ferromagnetic to paramagnetic temperatures. Data for increasing and decreasing fields at 2 K and 4 K intervals were collected, involves a range around the T_c , providing evidence for the absence of magnetic hysteresis loss effects, which are inherent in second-order magnetic transitions [16]. Furthermore, Figure 4 (c-d) depicts the corresponding Arrott plots (M^2 against B/M) for the MnCoGe and MnCoAl, demonstrating a typical second-order transition for both samples. This is supported by the lack of S-shaped behaviour of the Arrott plot at T_c , which indicates a positive sign of the coefficient in the magnetic free energy Landau expansion [11]. The magnetic entropy change, $-\Delta S_M$, has been determined from their magnetization curves for both increasing field and decreasing field values as functions of magnetic field ($\Delta B = 0$ –5 T) and temperature. $-\Delta S_M$ is calculated by using the standard Maxwell relation [3]:

$$-\Delta S_M(T, H) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H (dH) \quad (1)$$

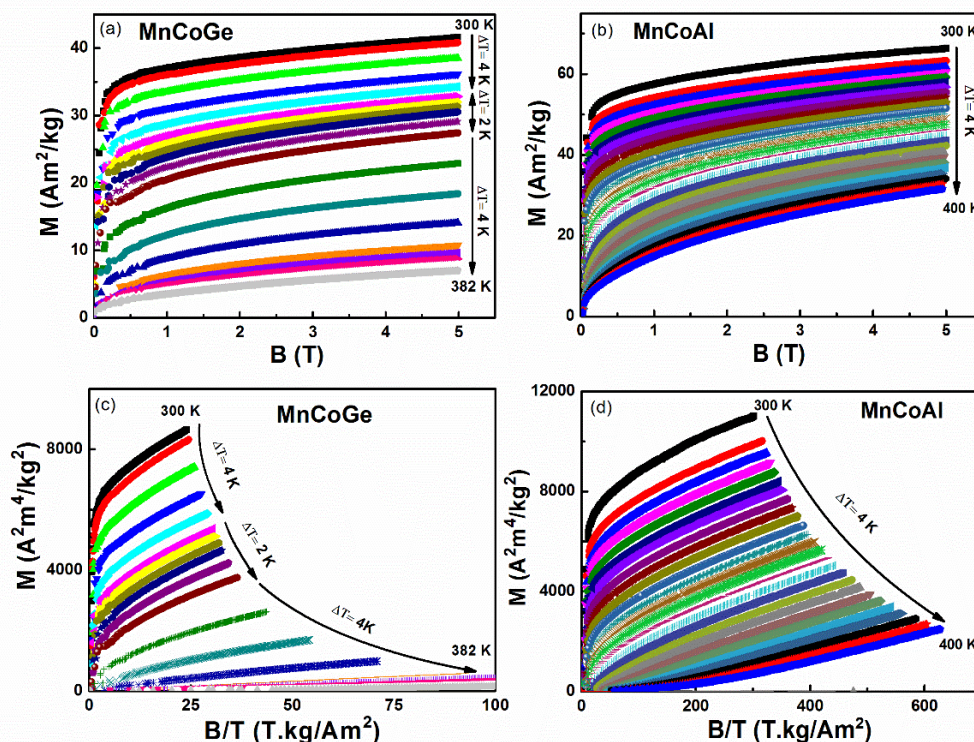


Figure 4. Magnetization isotherms with an applied field of 0-5 T for (a) MnCoGe compound and (b) MnCoAl compound; and (c, d) Arrott plots showing the second-order transition type for both compounds.

Even though there is uncertainty in using Maxwell's relation for first-order systems, Caron *et al.* have successfully utilized decreasing field method as a technique in determining the $-\Delta S_M$ of first-order systems [17]. $-\Delta S_M$ is calculated in both increasing and decreasing field mode, as illustrated by the closed symbol (increasing) and open symbol (decreasing) in Figure 5. The calculated $-\Delta S_M$ values show no difference for increasing and decreasing fields, confirming that no hysteresis loss occurred near the magnetic transition. The maximal values of the $-\Delta S_M$ are about 4.41 and 3.73 J·kg⁻¹·K⁻¹ for MnCoGe and MnCoAl, for a field change of 0-5 T, respectively.

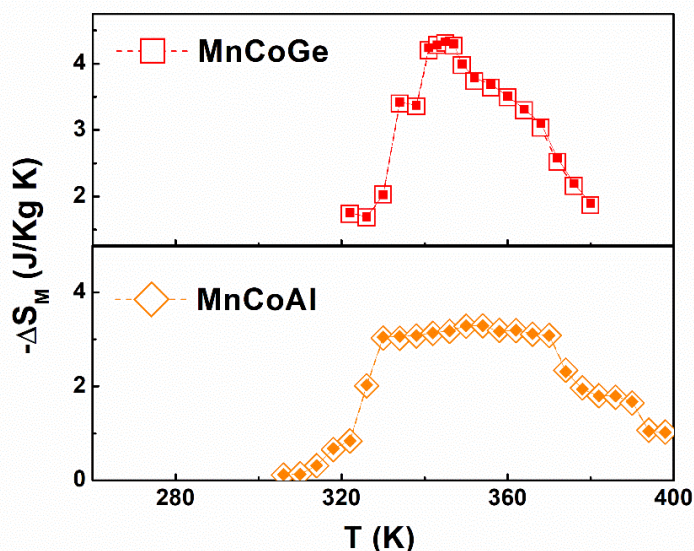


Figure 5. Temperature dependence of the isothermal magnetic entropy change, $-\Delta S_M(T, H)$, for MnCoGe and MnCoAl compounds calculated from magnetization isotherms with 0-5 T field change applied. The increasing field is represented by the closed symbols and the decreasing field is represented by open symbols.

4. CONCLUSION

In conclusion, the substitution of Al for Ge atoms has made changes in the structural transformation from an orthorhombic structure at MnCoGe to a hexagonal structure at MnCoAl at room temperature. For Curie temperatures, it was found that the T_c decreases from 340 K to 285 K with the substitution of Al with Ge. Besides, it was found that for MnCoAl, the T_{str} decreases and overlaps with the Curie temperature of the martensite phase which could contribute to large MCE.

Furthermore, the Arrott plots (M^2 against B/M) for the MnCoGe and MnCoAl, demonstrated characteristics of second-order transition for both samples. This is supported by the lack of S-shaped behaviour of the Arrott plot at T_c , which indicates a positive sign of the coefficient in the Landau expansion of the magnetic free energy. The calculated magnetic entropy change, $-\Delta S_M$ values shows no difference for increasing and decreasing fields, which confirms that there is no hysteresis loss occurred near the magnetic transition. The $-\Delta S_M$ maximal values is about 4.41 J·kg⁻¹K⁻¹ for MnCoGe and 3.73 J·kg⁻¹K⁻¹ for MnCoAl, for a field change of 0-5 T.

ACKNOWLEDGEMENTS

This work is supported partly by the Fundamental Research Grant Scheme (FRGS/1/2019/STG07/UPNM/02/7) and (FRGS/1/2015/SG06/UPNM/03/3) Ministry of Higher Education Malaysia. The authors thank the National Defence University of Malaysia for the financial support of this research.

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