Magnetostructural transitions in V-doped MnCoGe compounds

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ABSTRACT
MnCoGe\(_{1-x}V_x\) (\(x = 0.005, 0.01, 0.015, 0.02, 0.03,\) and 0.04) compounds were synthesized and investigated in view of the effect of transition metals on main-group-element sites to the magnetostructural transition. A small amount of V doping results in a decrease of the martensitic transformation temperature, while a further increase of V disturbs the Co-Ge bonds hence destabilizing the MM'X phase. Therefore, the transformation temperature returns to high temperature, and the expected Curie temperature window becomes incomplete. Accordingly, a large magnetic entropy change of about 10 J/kg K and a refrigerant capacity of about 129.5 J/kg is obtained in the series.

INTRODUCTION
So far, most studies on magnetic refrigeration are focused on materials undergoing a first-order magnetic phase transition due to their large magnetocaloric effect.\(^1\)-\(^7\) Amongst many kinds of such materials, the well-known MM'X family is particularly interesting for its unique 'Curie temperature window' (CTW) phenomenon.\(^8\) These compounds show a martensitic transformation from the high-temperature Ni\(_2\)In-type hexagonal structure to the low-temperature TiNiSi-type orthorhombic structure.\(^5\)-\(^10\) However, to the best of our knowledge, the structural transition (\(T_M\)) of the MM'X systems known so far occurs at higher temperatures than the Curie temperature of martensite (\(T_C^M\)), implying that they are not coupled together. Therefore, the priority in studying an MM'X compound is to tune its \(T_M\) into the CTW and hence the structure transition will occur from a paramagnetic hexagonal phase to a ferromagnetic orthorhombic phase and achieving the magnetostructural coupling. In the most intensively studied MM'X compound, i.e. MnCoGe, there are several effective ways to decrease the \(T_M\) from 650 K to room temperature and establish the CTW. Studies on Mn vacancy in MnCoGe systems show that Co atoms could fill in Mn vacancies, resulting in the appearance of Co vacancy and thus the \(T_M\) can be adjusted to lower temperatures.\(^1\) Apart from this method, introducing interstitial atoms\(^6\) or physical hydrostatic pressure\(^10,11\) in MnCoGe system can also effectively tune the structural transition temperature.

Recently, a new family of all-d-metal Heusler compounds with first-order magnetostructural transition has been discovered.\(^12,13\) In this system, the Ti or V atoms with a low number of valence electrons can form p-p hybridization with the other transition elements, playing the role of main group elements as those in conventional Heusler compounds. These works raise a new question about how will the transition elements behave on a main-group-element site. We know that in the MM'X compound, M' and X form a network of hexagons which is the basis of the crystal structure. The decrease of \(T_M\) usually depends on the weakening of these M'-X networks. Therefore, the effect of transition elements like Ti and V on the stability of the hexagonal net is a topic worthy of investigation.

In this study, we synthesized a series of MnCoGe\(_{1-x}V_x\) (\(x = 0.005, 0.01, 0.015, 0.02, 0.03,\) and 0.04) samples and investigated the effect of the transition element V on phase stability, structural transition, and magnetic behavior in the MnCoGe system.
EXPERIMENTAL PROCEDURE

The MnCoGe\(_{1-x}\)V\(_{x}\) (x = 0.005, 0.01, 0.015, 0.02, 0.03, and 0.04) alloys were prepared by melting the appropriate amounts of high purity constituent elements four times under an Ar atmosphere with arc melting. The ingots were then annealed at 1123 K for 5 days and cooled down to room temperature in oven naturally. The phase content and crystal structure of the samples were determined by X-ray diffraction (XRD) measurements at room temperature using Bruker D8 Advance diffractometer. The microstructure and element distribution of the samples were examined using scanning electron microscopy (SEM) and energy dispersive X-ray detector (EDX), respectively. The characteristic of the phase transition of the samples was performed using differential scanning calorimetry (DSC) on DSC-214 Polyma-Netzsch equipment with the heating and cooling rates of 10 K/min. The temperature dependences of the magnetization were carried out in the 100 ∼ 400 K temperature range under an applied field of 0.01 T, using a vibrating sample magnetometer (VersaLab, Quantum Design). The isothermal magnetization curves were measured around \(T_M\), under an applied field of up to 3T. Maxwell relations were used to calculate the magnetic entropy changes from isothermal magnetization curves (M-H). The values of the refrigerant capacity (RC) were calculated by numerical integration of the corresponding temperature dependences of magnetic entropy change, with the temperature at half-maximum values of the peak used as the integration limit.

RESULTS AND DISCUSSION

To identify the crystal structure, we performed XRD measurements at room temperature for all MnCoGe\(_{1-x}\)V\(_{x}\) compounds, as seen in Fig. 1. The patterns can be indexed as TiNiSi-type orthorhombic structure, coexisting with a small amount

![XRD pattern of MnCoGe\(_{1-x}\)V\(_{x}\) compounds](image)

**FIG. 1.** XRD pattern of MnCoGe\(_{1-x}\)V\(_{x}\) (x=0, 0.01, 0.015, 0.02, 0.03 and 0.04) compounds, in which the diffraction peaks of orthorhombic and hexagonal structures are marked with □ and •, respectively.

![DSC heat flow curves as a function of temperature for MnCoGe\(_{1-x}\)V\(_{x}\) compounds](image)

**FIG. 2.** DSC heat flow curves as a function of temperature for MnCoGe\(_{1-x}\)V\(_{x}\) (x=0, 0.01, 0.015, 0.02, 0.03 and 0.04) compounds. The dashed arrows denote the heating and cooling curves. \(T_{CM}\), \(T_{DSC}\), \(M_F\) (\(M_F\)) and \(A_S\) (\(A_F\)) are the Curie temperature of martensite, transformation temperature based on DSC curves, starting (finishing) temperature of martensitic transition and the starting (finishing) temperature of reversal martensitic transition, respectively.

| Samples           | \(T_C^M/T_M\) (K) | \(\Delta T_{HY}\) (K) | Maximum magnetic hysteresis loss (J/kg) | \(\Delta S_M\) (J/kg*K) | RC (J/kg) |
|-------------------|-------------------|----------------------|----------------------------------------|------------------------|-----------|
| MnCoGe            | 345/418           | 4                    | -                                      | 5.6                    | -         |
| MnCoGe\(_{0.99}\)V\(_{0.01}\) | 343/343          | 10                   | 11.1                                   | 7.3                    | 117.3     |
| MnCoGe\(_{0.85}\)V\(_{0.015}\) | 317              | 11                   | 16.7                                   | 10                     | 129.5     |
| MnCoGe\(_{0.98}\)V\(_{0.02}\) | 300              | 14                   | 11.8                                   | 7.1                    | 115.9     |
| MnCoGe\(_{0.97}\)V\(_{0.03}\) | 294              | 12                   | 10.9                                   | 6.3                    | 101.1     |
| MnCoGe\(_{0.96}\)V\(_{0.04}\) | 301              | 23                   | 5.8                                    | 3.9                    | 122.4     |

**TABLE I.** The transformation temperature \((T_M)\) or Curie temperature \((T_C)\), thermal hysteresis \((\Delta T_{HY})\), maximum magnetic hysteresis loss, maximum entropy change \((\Delta S_M)\) and refrigerant capacity \((RC)\) of the MnCoGe\(_{1-x}\)V\(_{x}\) compounds.
FIG. 3. Temperature dependence of magnetization ($M-T$ curves) measured at a field of 100 Oe with a rate of 3 K/min during heating and cooling for MnCoGe$_{1-x}$V$_x$ compounds. The inset shows the SEM image of the sample with $x = 0.04$ and the EDX composition of the second phase.

As the further increase of V, the hexagonal phase becomes dominant gradually, indicating that the martensitic transformation temperatures $T_M$ has been decreased to near room temperature.

To clarify the doping effect of V element on the phase transition of MnCoGe compound, we carried out DSC measurements, as shown in Fig. 2. For the parent phase with $x = 0$, there are two pairs of peaks, the low-temperature pair and the high-temperature pair, on heating and cooling curves. The high-temperature one is relatively strong and shows a large thermal hysteresis during heating and cooling, which could be attributed to the structural transitions between the hexagonal and orthorhombic phases ($T_M \approx 418$ K). The low-temperature pair of peaks have no obvious thermal hysteresis and can be identified as the $T_C$ of the orthorhombic phase ($T_C \approx 340$ K). With the introduction of V, $T_M$ is dramatically decreased from 418 K for $x = 0$ to around 340 K for $x = 0.01$, as seen in Table 1. Further increase of V leads to a gradual decrease of $T_M$ until $x = 0.03$. Starting from this composition, $T_M$ tends to be stable or even increase slightly. It implies that the effect of V doping is suspended or weakened. A more important phenomenon is the obvious of hexagonal phase for samples with $x = 0$, 0.01 and 0.015. As the further increase of V, the hexagonal phase becomes dominant gradually, indicating that the martensitic transformation temperatures $T_M$ has been decreased to near room temperature.

FIG. 4. Magnetization isotherms ($M-H$) curves of MnCoGe$_{1-x}$V$_x$ compounds with (a) $x = 0.01$, (b) $x = 0.015$, (c) $x = 0.02$, (d) $x = 0.03$, (e) $x = 0.04$ in a field change of 3T, and (f) magnetic hysteresis loss for all compounds.
reduction of the DSC peaks for the samples with $x = 0.03$ and $0.04$. It confirms that the first-order transition is largely suppressed. These phenomena may be explained by examining the magnetic behavior of these series.

Temperature dependence of the magnetization of MnCoGe$_{1-x}$V$_x$ compounds was measured in both cooling and heating processes, as seen in Fig. 3. The parent phase with $x = 0$ shows a single paramagnetic to ferromagnetic (PM-FM) transition with almost no thermal hysteresis, corresponding to the $T_{C}^{M}$. When doped with V, an evident thermal hysteresis first appears in the sample of $x = 0.01$ and expands gradually with the increase of V till $x = 0.02$. This suggests that the magnetostructural transition is achieved in the system by V doping. However, when $x = 0.03$ and $0.04$, the $T_{M}$ stops decreasing and returns to higher temperatures. In addition, the magnetization difference ($\Delta M$) is notably reduced for these two samples, which is caused by the remaining magnetization in the supposed paramagnetic range at high temperature. These results are consistent with the results of XRD and DSC, suggesting the existence of secondary magnetic phases.

The inset of Fig. 3 shows the SEM image of the $x = 0.04$ sample, in which one can see two distinct contrasts. The bright contrast belongs to the main MnCoGe phase, while the dark one corresponds to the second phase with less Ge than the matrix. Unfortunately, due to the relatively small amount of this second phase, it cannot be detected by XRD and thus difficult to be identified. However, considering the existence of Mn-Co-Ge(V) type of Heusler alloys and their relatively high Curie temperatures, one may infer that the second phase is an energetically favorable Heusler alloy containing Mn, Co, Ge, and V elements. Nevertheless, the existence of a second phase implies that the V element disturbs the network of Co-Ge bonds and causes the instability of the MM’X phase. This is understandable because the Co-Ge (i.e. M’-X) layers with strong and rigid covalent bonds are the framework of the MnCoGe (MM’X) compounds, while the doped V element has a weaker covalent effect than Ge. This will thus weaken the Co-Ge bond system, which in turn causes a decrease of $T_{M}$ and eventually the appearance of the second phase.

The field dependence of the magnetization of MnCoGe$_{1-x}$V$_x$ compounds was studied using isothermal magnetization ($M$-$H$) curves around $T_{M}$, as shown in Fig. 4 (a-e). The metamagnetic transition with hysteresis for all the compounds indicates that the magnetic field induced martensitic phase transition occurs in all the samples. Fig. 4 (f) shows magnetic hysteresis loss of different compositions at different temperatures. One can see that with the enhancement of magnetostructural coupling ($x = 0.0$ - 0.015), the magnetic hysteresis loss increases, while the weakening of it leads to the decrease of the magnetic hysteresis loss ($x = 0.015$ - 0.04).

The temperature dependence of the magnetic entropy change derived from the $M$-$H$ curves in Fig. 4 using Maxwell relation are shown in Fig. 5(a). The maximum entropy change ($\Delta S_{M}$) is 10 J/kg.K for the sample with $x = 0.015$. The values of the refrigerant capacity ($RC$) were calculated by numerical integration of the corresponding $\Delta S_{M}$-$T$ curves, with the temperature at half-maximum values of the peak used as the integration limit. The RC values are 117.3, 129.5, 115.9, 101.1 and 122.4 J/kg for $x = 0.01$, 0.015, 0.02, 0.03 and 0.04, respectively. Based on these results, the structural and magnetic phase diagram of MnCoGe$_{1-x}$V$_x$ system is created and shown in Fig. 5(b). Since the Mn sublattice is unaffected by V doping on Ge site, $T_{C}^{M}$ of MnCoGe should be treated as unchanged like in many related systems. Therefore, the expected CTW in the current system should be 68 K, considering that $T_{C}^{M}$ in the present system is 343 K. However, this value is decreased to 50 K eventually due to the existence of the second phase. If the second phase can be suppressed through different preparation methods like rapid solidification, the CTW can still be recovered. Nevertheless, the effect of V doping on Ge site is compared with those of other doping systems as shown in Table II. Therefore, this system has the potential to be a good magnetocaloric material and the doping effect of transition elements on the main group element site in MM’X materials is worthy of further investigation.
CONCLUSION

In summary, the structural and magnetic properties of MnCoGe\(_{1-x}\)\(V_x\) (\(x = 0.005, 0.01, 0.015, 0.02, 0.03,\) and \(0.04\)) compounds were investigated. The transition temperature \(T_M\) reduces with the substitution of \(V\) for \(Ge\) due to the decrease of the valence-electron concentration and weakening of the Co-Ge bond. \(T_M\) decreases from 343 K to 293 K when \(x\) goes from 0.01 to 0.03 and then it increases to 301 K when \(x = 0.04\). The reason is that a further increase of \(V\) disturbs the Co-Ge bonds, which in turn destabilizes the MM’X phase and leads to a second phase. Therefore, the transformation temperature returns to high temperature, and the expected Curie temperature window becomes incomplete. Accordingly, a large magnetic entropy change of about 10 J/kg/K and a refrigerant capacity of about 129.5 J/kg is obtained in the series. This work provides an effective choice for modulating the magnetosstructural transformation systems like MnCoGe in the MM’X family.

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| Compounds | \(T_M\) (K) | \(-\Delta S_M\) (J/kg K) | \(\Delta H\) (T) | CTW (K) | Ref. |
|-----------|-----------|-----------------|-------------|--------|-----|
| MnCoGe\(_{0.95}\)Sn\(_{0.05}\) | 280 | 4.5 | 0-1 | -60K | 4 |
| MnCoGe\(_{0.82}\) | 287 | 20 | 0-2 | -70K | 6 |
| MnCoGe\(_{0.78}\)Al\(_{0.2}\) | 324 | 22 | 0-3 | -80K | 18 |
| MnCoGe\(_{0.81}\)Sn\(_{0.1}\) | 350 | 2.9 | 0-2 | -96K | 19 |
| MnCoGe\(_{0.95}\)Ge\(_{0.05}\) | 317 | 20 | 0-3 | -80K | 20 |
| MnCoGe\(_{0.97}\) | 324 | 21 | 0-3 | -76K | 21 |
| MnCoGe\(_{1.02}\) | 305 | 20 | 0-3 | -70K | 22 |
| MnCoGe\(_{0.95}\)V\(_{0.05}\) | 317 | 10 | 0-3 | -50K | This work |

TABLE II. The \(T_M\), \(-\Delta S_M\) values corresponding to field change \(\Delta H\), and the Curie temperature window (CTW) of different doping systems.
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