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Windows open for highly tunable magnetostructural phase transitions

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An attempt was made to tailor the magnetostructural transitions over a wide temperature range under the principle of isostructural alloying. A series of wide Curie-temperature windows (CTWs) with a maximal width of 377 K between 69 and 446 K were established in the Mn1−yCyNiGe1−xSix system. Throughout the CTWs, the magnetic-field-induced metamagnetic behavior and giant magnetocaloric effects are obtained. The (Mn,Co)Ni(Ge,Si) system shows great potential as multifunctional phase-transition materials that work in a wide range covering liquid-nitrogen and above water-boiling temperatures. Moreover, general understanding of isostructural alloying and CTWs constructed in (Mn,Co)Ni(Ge,Si) as well as (Mn,Fe)Ni(Ge,Si) is provided.

Magnetic materials with considerable caloric effects in the vicinity of magnetoelastic or magnetostructural transitions (MSTs) show great potential in solid-state refrigeration.1–3 Currently, a large number of caloric materials have been successively found, including the magnetocaloric materials working at different temperatures.4 Tunable magnetocaloric effects (MCEs) over a wide temperature range may provide expended chance for different applications. Especially, high-temperature MCEs, which may be used at elevated temperatures especially above water boiling point (373 K) for magnetic heat pumps,5 electric power generation,6,7 or magnetic cooling8,9 are seldom reported.

In recent years, hexagonal MM′X (M, M′ = transition metals, X = carbon or boron group elements) compounds have been extensively investigated due to the tunable MSTs and associated giant MCEs.10–12 In these MM′X compounds, the MSTs, from Ni2-In-type hexagonal parent phase to TiNiSi-type orthorhombic martensite with different magnetic states, can be obtained by coupling martensitic structural transitions (MTs) with magnetic transitions. The Curie-temperature windows (CTWs),12,14 constructed by Curie temperatures of parent (T_C^A) and that of martensite (T_C^M) phases, were revealed and used to maximize the magnetic-energy change in magnetic-field-induced MSTs. Many MSTs have been tuned into CTWs and exhibited remarkable magnetoresponsives effects.12–20 During the practice of MST tuning, we further proposed a principle of isostructural alloying to manipulate the structural transitions and the magnetic couplings at one time.14 The chemically substituting elements were determined from the viewpoint of alloying the isostructural counterparts before performing the experiments. Till now, CTWs have been established in many alloy systems,21–27 in which the tunable MSTs with giant MCEs were obtained.

Note: Invited for the Caloric Materials special topic.

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In our previously reported results, broad CTWs have been constructed by using isostructural alloying in both Mn$_{1-y}$Fe$_y$NiGe and Mn$_{1-y}$Co$_y$NiGe systems. By further applying isostructural alloying to Mn$_{1-y}$Fe$_y$NiGe and MnNiSi, an unprecedentedly wide CTW of 400 K has been achieved. According to the principle of isostructural alloying, a proper isostructural counterpart with a MT and a T$_C$M both at high temperatures should be selected to tune MSTs of Mn$_{1-y}$Fe$_y$NiGe to high temperatures. This is why MnNiSi was chosen, whose MT temperature (T$_M$) and T$_C$M are as high as 1200 K and 622 K, respectively. In Mn$_{1-y}$Co$_y$NiGe system, by doping Co atoms at Mn sites, a 230-K CTW from room temperature to 120 K was opened by simultaneously decreasing the MTs and converting the spiral antiferromagnetic (AFM) martensite to ferromagnetic (FM) state. Within the CTW, a giant MCE of $-40$ J kg$^{-1}$ K$^{-1}$ in a field change of 50 kOe was observed around 236 K for $y = 0.1$. The strongest ferromagnetism of martensite phase was obtained near 120 K for $y = 0.2$. Unfortunately, the desired magnetoresponsive properties disappear for $y > 0.2$ because the MST vanishes below 120 K when it meets T$_C^\lambda$. In the MMX family, there exists an interesting phenomenon that the MT vanishes suddenly when it encounters T$_C^\lambda$, which means that the ferromagnetic ordering at T$_C^\lambda$ will suppress the MTs. For the case in Mn$_{1-y}$Co$_y$NiGe, it is possible to isostructurally alloy MnNiSi with Mn$_{1-y}$Co$_y$NiGe, to (i) simultaneously increase T$_M$ and T$_C$M and (ii) lower T$_C^\lambda$. For the compositions with higher Co-contents, T$_C^\lambda$ of Mn$_{1-y}$Co$_y$NiGe would be decreased to low temperatures as the paramagnetic CoNiGe destroys the FM coupling of MnNiGe parent phase. By doing these, an expanded CTW for tunable MSTs becomes hopeful.

In this work, taking MnNiSi as an isostructural counterpart we create an Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ ($y = 0.2; 0 \leq x \leq 1$) system by simply substituting Si for Ge in Mn$_{1-y}$Co$_y$NiGe. The compositions with higher Co-contents ($y = 0.3, 0.4$) are also taken into account. The obtained MSTs can be highly tuned in a wide temperature range from 70 to 450 K. More importantly, in the present paper general discussions and summaries on this work and some previous works are made.

Polycrystalline ingots of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ ($y = 0.2, 0.3, 0.4; 0 \leq x \leq 1$) alloys were prepared by arc melting high-purity metals four times in argon atmosphere. All ingots were annealed at 1123 K in an evacuated quartz tube for five days and then cooled slowly to room temperature. The phase structures of the samples were characterized by powder x-ray diffraction (XRD) with Cu-K$_\alpha$ radiation. The differential scanning calorimetry (DSC) with permanent-magnet assisted thermogravimetric analysis (TGA) was used to detect the structural and magnetic transitions. With the aid of the upward magnetic pull forces provided by the magnets, a change in sample weight can be detected across the magnetic transition by TGA. The magnetic measurements were performed on superconducting quantum interference device (SQUID) magnetometer, physical property measurement system (PPMS) in the range of 5–400 K, as well as the vibrating sample magnetometer (VSM, VersaLab, 3 T) for temperatures above 400 K.

Room-temperature XRD analyses of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ system were performed. Figure 1(a) shows the lattice parameters of Mn$_{0.8}$Co$_{0.2}$NiGe$_{1-x}$Si$_x$ ($0 \leq x \leq 0.45$) samples obtained from XRD patterns (Figure S1 and Table S1 in the supplementary material). Mn$_{0.8}$Co$_{0.2}$NiGe ($x = 0$) shows a Ni$_3$In-type hexagonal structure, which is consistent with our previous study. Mn$_{0.8}$Co$_{0.2}$NiGe$_{1-x}$Si$_x$ series crystallize in a Ni$_3$In-type hexagonal structure for $x \leq 0.25$ and a TiNiSi-type orthorhombic structure for $x \geq 0.30$, which indicates that T$_M$ rises from low temperature to above the room temperature. With increasing Si content, the cell volumes of both hexagonal and orthorhombic phases decrease due to the smaller size of Si than Ge atom. As shown in Fig. 1(a), large volume expansions of 2.5% and 2.3% during the MT are observed, respectively, for $x = 0.25$ and 0.30, which are consistent with those obtained by temperature-dependent XRD in similar hexagonal alloys.

The M(T) curves of Mn$_{0.8}$Co$_{0.2}$NiGe$_{1-x}$Si$_x$ ($x = 0.10, 0.15, 0.25, 0.35$) alloy series in a field of 1 kOe between 5 K and 400 K were measured, as shown in Fig. 1(b). For Mn$_{0.8}$Co$_{0.2}$NiGe ($x = 0$), the first-order MST from the FM parent to FM martensite state, with a clear thermal hysteresis below T$_C^\lambda \sim 129$ K, occurs at 93 K upon cooling (determined as maximal dM/dT). Once Si is introduced on Ge site, MT temperature T$_M$ begins to rise, similar to what is observed in Mn$_{1-y}$Fe$_y$NiGe$_{1-x}$Si$_x$. The tunable first-order MSTs, happening from paramagnetic (PM) hexagonal parent to FM orthorhombic martensite phase, are obtained in alloys with $x$ from 0.10 to 0.35. The highest-temperature MST is observed at 364 K for $x = 0.35$. As shown in Fig. 1(c), the M(T) curves of Mn$_{0.8}$Co$_{0.4}$NiGe$_{1-x}$Si$_x$ ($0.45 \leq x \leq 0.85$) samples in a field of 1 kOe are presented. For
FIG. 1. Si-content dependence of (a) room-temperature XRD patterns and cell volumes of hexagonal and orthorhombic phases of Mn$_{0.8}$Co$_{0.2}$NiGe$_{1-x}$Si$_x$. There is a relation between volumes of hexagonal ($V_h$) and orthorhombic ($V_o$) phases: $V_o \sim 2V_h$, $\Delta V/V_h = (V_o - 2V_h)/2V_h$. (b) Temperature dependence of the magnetization ($M(T)$ curves) in the field of 1 kOe of Mn$_{0.8}$Co$_{0.2}$NiGe$_{1-x}$Si$_x$. (c) $M(T)$ curves in the field of 1 kOe of Mn$_{0.6}$Co$_{0.4}$NiGe$_{1-x}$Si$_x$. $x = 0.45$, no structural transition occurs and only a weak magnetic transition is seen at 69 K. When $x$ is increased to 0.50, the MST recurs suddenly at 93 K, showing a first-order PM-FM transition. For $x \geq 0.50$, $T_t$ increases steadily, spanning over a large temperature range, finally reaches 429 K, and $T_{CM}$ appears at 446 K when $x = 0.85$.

Based on all data from XRD, magnetic, and DSC-TGA measurements (Figs. S1 and S2 in supplementary material), we propose a magnetostructural phase diagram (see complete phase diagram in Fig. S3) of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ ($y = 0.2, 0.3, 0.4; 0 \leq x \leq 1$), as shown in Fig. 2(a). For all alloy series, the transition temperature $T_t$ can be raised to high temperatures by Si substitution and encounters $T_{CM}$ (also upper critical temperature, $T_{cr}$) at high temperatures of 409 K, 429 K, and 446 K for $y = 0.2, 0.3, 0.4$, respectively. With increasing Co content ($y$), at the same time the $T_{CA}$ (also lower critical temperature, $T_{cr}$) of CTW decreases from 125 K to 69 K. These behaviors are consistent with those in Mn$_{1-y}$Fe$_y$NiGe$_{1-x}$Si$_x$ system. This brings about an encouraging result that the width of the CTW between upper and lower $T_{cr}$ is increased from 230 K to 377 K. The broad and extended CTW series are realized in Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ system.

According to our previous study, high Co content can highly stabilize the parent phase of Mn$_{1-y}$Co$_y$NiGe since the isostructural counterpart CoNiGe has a stable parent structure, as shown in Fig. 2(b). In principle, higher Co content would bring the MT to very low temperatures, even below the absolute temperature if Co content is high enough. In order to gain a complete and deep understanding on the magnetostructural transitions in alloy series with higher Co contents ($y > 0.2$), we extrapolated the real transition temperatures above $A_0$ point ($T_t \sim 93$ K of Mn$_{0.8}$Co$_{0.2}$NiGe compound) to get the theoretical martensitic transition temperature $T_t$, as shown by the broken line. For the studied $y = 0.3$ and 0.4, the theoretical $T_t$ reaches to $B_0$ and $C_0$ points respectively, where the parent phase has been deeply stabilized. Owing to high $T_t$ of MnNiSi, introducing Si can weaken the stability of parent phase and immediately raise $T_t$ of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$, as demonstrated by the case of $y = 0.2$ alloy series in Figs. 2(a) and 2(b). The theoretical $T_t$ of $y = 0.3$ and 0.4 alloy...
FIG. 2. Magnetostructural phase diagram of (a) \( \text{Mn}_{1-y}\text{Co}_{y}\text{NiGe}_{1-x}\text{Si}_{x} \) \((y = 0.2, 0.3, 0.4; 0 \leq x \leq 1) \) and (b) \( \text{Mn}_{1-y}\text{Co}_{y}\text{NiGe} \) \((0 \leq y \leq 0.2) \) system with wide Curie-temperature windows (CTWs), by introducing the Si and Co elements based on the isostructural alloying principle, respectively. The light yellow region demonstrates the region of CTWs between \( T_{\text{CM}} \) and \( T_{\text{CA}} \).

series will also increase from \( B_{0} \) and \( C_{0} \), respectively, to higher temperatures. With the parent phase being stabilized deeply, nevertheless, it needs more Si contents \((x = 0.26 \) for \( y = 0.3 \) and \( x = 0.48 \) for \( y = 0.4 \)) to awaken the “dead” transition above \( T_{\text{CA}} \) (the lower \( T_{\text{cr}} \), denoted by \( A_{1}, B_{1}, \) and \( C_{1} \) in Fig. 2(a)). As mentioned above, for \( \text{MM}'X \) compounds the magnetic ordering around \( T_{\text{CA}} \) can suppress the MTs.\,\,\,\,12,14,16,32\) Higher Co content results in a decrease in \( T_{\text{CA}} \) from 125 K to 69 K, due to the paramagnetism of isostructural CoNiGe.\,\,\,33\) The transitions can be thus observed at lower temperatures where the suppression is removed. In this case, Co substitution at Mn sites provides a larger temperature space for Si substitution to raise the MST (for example, from \( B_{1} \) to \( B_{2} \)). For high Si contents, \( T_{\text{CM}} \) (the upper \( T_{\text{cr}} \)) of the system is increased from 409 K \((A_{2}) \) to 446 K \((C_{2}) \) because of the high \( T_{\text{CM}} \) of MnNiSi counterpart. The combined effects of Co- and Si- substitution from the view of isostructural alloying thus lead to a series of broad CTWs for highly tunable MSTs.

From the results, one can see that for MnNiX based compounds introducing Co at Mn sites plays an essential role in keeping \( T_{\text{CA}} \) (the lower \( T_{\text{cr}} \)) of the studied systems at low temperatures. This situation is also applicable to \( \text{Mn}_{1-y}\text{Fe}_{y}\text{NiGe} \),\,\,\,14\) \( \text{Mn}_{1-y}\text{Fe}_{y}\text{NiGe}_{1-x}\text{Si}_{x} \),\,\,\,28\) and \( \text{Mn}_{0.5}\text{Fe}_{0.5}\text{NiSi}_{1-x}\text{Al}_{x} \),\,\,\,23\) systems in which Fe atoms were also introduced to Mn sites. Only in this case can the CTW that covers low temperatures be established and can the MSTs be tuned to low temperatures without suppression by the magnetic ordering of parent phase. Meanwhile, Co or Fe at Mn sites plays a key role in keeping the strong FM coupling in martensite, which is quite important in MnNiX based compounds. In contrast, due to the high \( T_{\text{CA}} \) of isostructural counterparts MnCoGe (260 K) and MnFeGe (228 K), introducing Co or Fe at Mn sites always makes \( T_{\text{CA}} \) of the studied systems such as \( \text{MnNi}_{1-x}\text{Fe}_{x}\text{Ge} \) very high,\,\,\,25,28,35\) which narrows the CTWs and constrains the MSTs at high temperature range. Nowadays, almost all the MSTs of \( \text{MM}'X \) compounds are studied within the CTWs, in order to get large magnetization changes and desired properties. During the composition design, it is necessary to pay more attention to this difference of atom occupying sites and the atom-resolved magnetic exchange interactions, which is an important base for accurate applications of the so-called isostructural alloying principle.\,\,\,14,21,28\) Confusion of site difference and negligence of CTW will lead to inefficient results or even wrong conclusions, like the case in Ref. 36. Here it should be further stated that, if the alloys are in equilibrium state Co (Fe) atoms prefer the Mn sites than Ni sites in \( \text{Mn}_{1-y}\text{Co}_{y}\text{NiGe}_{1-x}\text{Si}_{x} \) \((\text{Mn}_{1-y}\text{Fe}_{y}\text{NiGe}_{1-x}\text{Si}_{x}) \) system, which is dominated by the atom site occupation (valence electron) rule of \( \text{MM}'X \) compounds.\,\,\,14,21,37,38
In order to further analyze the ferromagnetism behavior within the broad CTWs obtained in this study, we measured the magnetization M(H) curves of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ samples ($y = 0.2, 0.3, 0.4; 0 \leq x \leq 1$) at 5 K. The related $M_S$ and $H_C$ are shown in Fig. 3. For Mn$_{1-y}$Co$_y$NiGe series ($x = 0$), with increasing Co content the martensite phase changes from the spiral AFM state with a high saturation field ($H_s$) of about 100 kOe to a FM state with a relatively low $H_s$ of about 2.9 kOe, as shown in Inset I of Fig. 3. For Mn$_{0.8}$Co$_{0.2}$NiGe$_{1-x}$Si$_x$ ($y = 0.2$) series, after introducing Si to the system the $H_s$ further decreases from 2.9 kOe ($x = 0$) to 1.74 kOe ($x = 0.45$). Inset II of Fig. 3 depicts the magnetization curve at 5 K of an example alloy with $y = 0.2$ and $x = 0.20$, showing a typical FM behavior with a low $H_s$, which is desired for the low-field effects. At the same time, $M_s$ of this alloy series remains basically unchanged with high values of 70–80 emu g$^{-1}$, which benefits the large magnetization change ($\Delta M$) across MSTs. For higher Co content of $y = 0.3$ and 0.4, similar trends are observed. Stable values of $M_s$ are maintained during the Si substitution, which can be attributed to the slight influence of the main-group elements in Ni-(Ge,Si) covalent networks.

All samples exhibit a negative (conventional) $\Delta S_f$ because the martensite is FM and the austenite is PM. Figures 4(c) and 4(d) show the MCEs of samples with $x = 0.10$ and 0.25 in Mn$_{0.8}$Co$_{0.2}$NiGe$_{1-x}$Si$_x$ series, for both samples, giant MCEs with $-35$ and $-40$ J kg$^{-1}$ K$^{-1}$ at a field change of 50 kOe are obtained. In particular, the MCEs at a low field of 20 kOe are also very large with values up to $-19$ and $-16$ J kg$^{-1}$ K$^{-1}$. These values are comparable with or even larger than many other MCE materials.

The (low-field) giant MCEs in the CTWs are mainly attributed to the low $H_s$ and high $M_s$ of the FM martensite phase (Fig. 3). Similarly, Figures 4(e) and 4(f) show the MCEs of samples with $x = 0.65$ in Mn$_{0.3}$Co$_{0.7}$NiGe$_{1-x}$Si$_x$ ($y = 0.3, x = 0.65$) and $x = 0.70$ in Mn$_{0.4}$Co$_{0.6}$NiGe$_{1-x}$Si$_x$ ($y = 0.4, x = 0.70$) series. Large MCEs of $-8$ and $-10$ J kg$^{-1}$ K$^{-1}$ at a field change of 30 kOe are respectively obtained. For the sample ($y = 0.3, x = 0.65$), in particular, the large, high-temperature MCE happens around 445 K. This temperature is much higher than those of many giant MCE materials. The large MCEs based on the highly tunable MSTs in the wide temperature range can be expected to provide a potential for wide-temperature-range applications, including the high-temperature magnetic cooling, magnetic heat pumps, and electric power generation above 400 K.
FIG. 4. Isothermal magnetization curves as a function of magnetic field at various temperatures of (a) \((y = 0.2, x = 0.10)\), (b) \((y = 0.2, x = 0.25)\). Isothermal entropy changes \((\Delta S_t)\) in various field changes of (c) \((y = 0.2, x = 0.10)\), (d) \((y = 0.2, x = 0.25)\), (e) \((y = 0.3, x = 0.65)\), (f) \((y = 0.4, x = 0.70)\).

A remarkable characteristic of MM’X alloys is their large volume expansion upon MSTs. As shown in Fig. 5, Mn_{1−y}Co_{y}NiGe_{1−x}Si_{x}, combined with Mn_{0.965}CoGe, MnNi_{0.8}Fe_{0.2}Ge, and Mn_{1−y}Fe_{y}NiGe_{1−x}Si_{x}, shows large volume expansion \((\Delta V/V)\) with 2.2% to 4% during MSTs. In other words, Si substitution almost does not reduce the large volume change during MSTs. The uniaxial strains along ch \((\varepsilon_h)\) reach 11.2% for Mn_{1−y}Co_{y}NiGe_{1−x}Si_{x} (Fig. 1(a)) and 12.4% for Mn_{1−y}Fe_{y}NiGe_{1−x}Si_{x}. The large \(\Delta V/V\) may enhance the MCEs that originated from magnetic and structural entropy changes. At the same time, these large \(\Delta V/V\) and uniaxial strain may bring considerable mechanocaloric effects (mCEs) including barocaloric and elastocaloric effects. Figure 6 shows the latent heats \((\Delta E)\) during MTs for the Mn_{1−y}Co_{y}NiGe_{1−x}Si_{x} and Mn_{1−y}Fe_{y}NiGe_{1−x}Si_{x} systems, which are rather large among the materials with first order transitions. The large \(\Delta E\) and the relatively small heat capacity \((C_p, \text{around } 1.4 \text{ J g}^{-1} \text{ K}^{-1})\) of this kind of material will lead to large adiabatic temperature change associated with MSTs. For the MST from PM parent phase to FM martensite phase in the present system, the two entropy changes enhance the total entropy change because they are both negative.
In summary, we have established a series of wide Curie-temperature windows that cover the temperature range from the cryogenic (70 K), through the room (300 K), and to the high temperatures (450 K) in single-phase Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ system, by simultaneously declining T$_{tA}$ and upraising both T$_t$ and T$_{CM}$ of the system under the principle of isostructural alloying. The first-order magnetostructural transitions can be highly tuned in the quite large temperature range. The giant entropy changes as large as $-40$ J kg$^{-1}$ K$^{-1}$ at 50-kOe field change are observed at 295 K. In particular, a high-temperature large entropy change of $-8$ J kg$^{-1}$ K$^{-1}$ at 30-kOe field change is gained near 450 K. Based on these magnetostructural transitions in the windows, the large MCEs, high-temperature MCEs, high tunability, large volume expansion, and uniaxial strain jointly make the (Mn,Co)Ni(Ge,Si) system of great potential for solid state cooling, heat pumps, functional gradient materials, energy conversion in different temperature regions. The principle of isostructural alloying and Curie-temperature window have shown the effectivity as a guideline in tuning structural and magnetic transitions and in designing magnetostructural materials.

Note added in proof: Our work is in agreement with a related study of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ (J. Liu et al., Sci. Rep. 6, 23386 (2016)), where $y = x$. 

FIG. 5. Volume expansion ($\Delta V/V$) of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$, Mn$_{1-y}$Fe$_y$NiGe$_{1-x}$Si$_x$, and some typical MM’X alloys with MSTs.$^{12,14}$

FIG. 6. Latent heat ($\Delta E$) during MSTs of Mn$_{1-y}$Co$_y$NiGe$_{1-x}$Si$_x$ and Mn$_{1-y}$Fe$_y$NiGe$_{1-x}$Si$_x$ systems.
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29. See supplementary material at http://dx.doi.org/10.1063/1.4955214 for structural and thermal analysis of Mn$_{1−x}$Co$_x$Ni$_{3−x}$Ge$_2$Si$_x$ and complete phase diagram of Mn$_{1−x}$Co$_x$Ni$_{3−x}$Si$_x$.