Coexisting Multiple Martensites in Ni_{57}−xMn_{21}+xGa_{22} Ferromagnetic Shape Memory Alloys: Crystal Structure and Phase Transition

Lian Huang 1, Daoyong Cong 2,*, Mingguang Wang 3 and Yadong Wang 2,*

1 Hunan Provincial Key Laboratory of Vehicle Power and Transmission System, Hunan Institute of Engineering, Xiangtan 411101, China; huanglianfriend@163.com
2 State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, No.30 Xueyuan Road, Haidian District, Beijing 100083, China
3 College of Sciences, Northeastern University, Shenyang 110819, China; wangmg@imp.neu.edu.cn
* Correspondence: dycong@ustb.edu.cn (D.C.); ydwang@ustb.edu.cn (Y.W.)

Abstract: A comprehensive study of the crystal structure and phase transition as a function of temperature and composition in Ni_{57}−xMn_{21}+xGa_{22} (x = 0, 2, 4, 5.5, 7, 8) (at. %) magnetic shape memory alloys was performed by a temperature-dependent synchrotron X-ray diffraction technique and transmission electron microscopy. A phase diagram of this Ni_{57}−xMn_{21}+xGa_{22} alloy system was constructed. The transition between coexisting multiple martensites with monoclinic and tetragonal structures during cooling was observed in the Ni_{57}−xMn_{21}+xGa_{22} (x = 5.5) alloy, and it was found that 5M + 7M multiple martensites coexist from 300 K to 160 K and that 5M + 7M + NM multiple martensites coexist between 150 K and 100 K. The magnetic-field-induced transformation from 7M martensite to NM martensite at 140 K where 5M + 7M + NM multiple martensites coexist before applying the magnetic field was observed by in situ neutron diffraction experiments. The present study is instructive for understanding the phase transition between coexisting multiple martensites under external fields and may shed light on the design of novel functional properties based on such phase transitions.

Keywords: magnetic shape memory alloy; martensitic transformation; external-field-induced structural transformation

1. Introduction

NiMn-based Ni-(Co)-Mn-Z (Z = Ga, In, Sn, Sb) Heusler-type alloys have fascinating multifunctional properties, such as magnetic-field-induced strain (MFIS) [1,2], super-elasticity [3,4], the magnetocaloric effect [5,6], the magnetoresistance effect [7] and magneto-thermal conductivity [8]. During the past two decades, intensive attention has been devoted to these multifunctional alloys due to their great potential for applications in magnetic sensing and actuation and magnetic refrigeration [9–12].

It is commonly recognized that the large MFIS in Ni-Mn-Ga alloys originates from the rearrangement of martensite variants (RMV) via the motion of twin boundaries under external fields; that is, one variant grows at the expense of others under an applied magnetic field [1]. However, this mechanism usually results in completely irreversible shape changes. On the other hand, an alternative actuation mechanism was also determined by Kainuma et al. [3]. This mechanism is correlated with the reverse martensitic transformation under an external field in Ni-(Co)-Mn-In alloys. Multifunctional properties can be
obtained by triggering the transformation between austenite and martensite by a magnetic field. Compared with RMV, this mechanism can bring about a reversible phase transformation, but the required magnetic field for this is usually larger than 5 T; this finding was confirmed by our group using a high energy X-ray diffraction technique [13], which is still quite high for practical applications using permanent magnets. This finding has inspired research into the exploration of other new mechanisms.

In fact, it was found that materials with compositions near the morphotropic phase boundary (MPB), a composition boundary between two different crystal structures in ferroelectric and ferromagnetic systems [14–16], can be extremely sensitive to external fields and exhibit enhanced physical properties under a low external field because the free energy difference between different structures at the MPB is so small that switching between different structures can be easily realized by an applied external field (electric or magnetic field) [14]. Since ferro-elastic (martensitic phase) systems are physically parallel to ferroelectric and ferromagnetic ones, it is expected that applying a low external field (stress or magnetic field) could also induce a transformation between coexisting multiple martensites, similar to the MPB cases in ferroelectric and ferromagnetic systems. Therefore, it is of great interest to search experimentally for coexisting multiple martensites in Ni-(Co)-Mn-Ga multifunctional alloys and investigate their structural evolution under a low external field.

It is well known that in Ni-(Co)-Mn-Ga multifunctional alloys, depending on the composition, temperature or mechanical stress, the parent L21 ordered cubic phase can transform to three different martensitic structures: five-layered (5M) [17–19] or seven-layered (7M) [2,19] modulated monoclinic martensite structure, or a non-modulated (NM) tetragonal martensite structure [19–21]. A multistep super-elastic behaviour is reported under an external field [9,20]. Therefore, by optimizing the composition or heat treatment, two or more coexisting martensites can be obtained due to their close formation energy; thus, applying a small external field (e.g., temperature, stress, or a magnetic field) can result in transformations between these coexisting martensites in such physically parallel ferro-elastic systems, which may yield a high output of functional properties (such as a giant magnetocaloric effect, large magnetoresistance and large MFIS) with a very low field [14].

In the present work, the crystal structure and phase transitions in Ni57−xMn21−xGa22 (x = 0, 2, 4, 5.5, 7, 8) (at. %) alloys were systematically investigated using calorimetry, magnetization and diffraction techniques as well as transmission electron microscopy (TEM). The obtained data enabled us to construct a phase diagram of this interesting multifunctional system. Furthermore, temperature-dependent synchrotron high-energy X-ray diffraction studies were performed to confirm the transition between coexisting multiple martensites with monoclinic and tetragonal structures during cooling in the alloy, with x = 5.5. Finally, an in situ neutron diffraction technique was employed to study the structural evolution of coexisting multiple martensites under a magnetic field at 140 K. These results will be instructive for designing novel magnetic shape memory alloys with low-field-triggered multifunctional properties.

2. Experimental

A series of polycrystalline ingots with a composition of Ni57−xMn21−xGa22 (x = 0, 2, 4, 5.5, 7, 8) (at. %) were prepared by repeated melting in an arc furnace under an argon atmosphere. Subsequently, each was sealed in an evacuated quartz tube and annealed at 1273 K for 4 h followed by water quenching to ensure homogeneity. Hereafter, the Ni57−xMn21−xGa22 alloys with x = 0, 2, 4, 5.5, 7, and 8 will be denoted as Ga22-1, Ga22-2, Ga22-3, Ga22-4, Ga22-5 and Ga22-6, respectively.

The phase transformation temperatures were measured by differential scanning calorimetry (DSC) in the temperature range of 223–473 K with cooling and heating rates of 10 K/min. Some of the bulk samples were crushed into fine powders for the synchrotron
high-energy X-ray diffraction (HEXRD) experiments. To remove the internal stress introduced during crushing, the powders were annealed at 850 K for 2 h. Temperature-dependent HEXRD experiments were carried out at the 11-ID-C beamline at the Advanced Photon Source, Argonne National Laboratory, USA. The diffraction Debye rings were collected by a two-dimensional (2D) image plate detector. A monochromatic X-ray beam with energy of ~115 keV was used.

In-situ neutron diffraction experiments were carried out on the high intensity diffractometer WOMBAT at the Australian Nuclear Science and Technology Organisation (ANSTO) [22]. For the in-situ measurements, WOMBAT was equipped with a vertical field magnet (field range: 0–11 T) with temperature range of 1.5–300 K. A wavelength of $\lambda = 2.41 \, \text{Å}$ was used for the measurements. A sample with the size of $\Phi 6 \times 15 \, \text{mm}$ was used, glued to a pure aluminium bolt.

Conventional TEM experiments were performed to study the microstructure and crystal structure of the martensites at room temperature. Thin foil samples for TEM observation were first mechanically ground to approximately 80 µm thick, followed by dimpling and ion-milling at 5 kV. The magnetic properties were measured in a physical property measurement system (PPMS, Quantum Design, San Diego, USA) with a magnetic field up to 14 T.

3. Results and Discussion

3.1. Composition Dependence of Phase Transformation Temperature and Curie Temperature

Based on DSC and magnetic measurements, the composition dependence of the phase transformation temperature and Curie temperature for Ni$_{57-}\text{Mn}_{21+}\text{Ga}_{22}$ ($x = 0, 2, 4, 5.5, 7, 8$) (at. %) is shown in Figure 1. The martensitic transformation temperatures $M_s$, $M_f$, $A_s$ and $A_f$ decrease with increasing $x$. The Curie temperature ($T_c$) of austenite is nearly constant ($\approx 369$ K), whereas the $T_c$ of martensite shows a tendency to increase along with increasing $x$. In particular, in the case of $x = 4$ (Ga$_{22}$-3), the martensitic and magnetic transitions occur simultaneously, suggesting the coupling between magnetic and structural transformations. Such a coupling is beneficial for obtaining large magnetocaloric effects due to the large magnetization difference between austenite and martensite (a panel of DSC curve to the Ga$_{22}$-3 alloy). It is believed that the martensitic transformation temperatures are dependent on the valence electron concentration ($e/a$) [23]. In our Ni$_{57-}\text{Mn}_{21+}\text{Ga}_{22}$ alloys, the martensitic transformation temperatures decrease with the decrease of $e/a$ caused by the substitution of Mn for Ni; this is in accordance with the previous reports on Ni–Mn–Ga alloys [24].
3.2. Evolution of the Crystal Structure for Ni_{57−x}Mn_{21+x}Ga_{22} Alloys

To examine the crystal structure evolution in the Ni_{57−x}Mn_{21+x}Ga_{22} alloys, temperature-dependent HEXRD experiments were performed. According to previous studies [24], Ni-Mn-Ga alloys with high transformation temperatures always undergo a first-order martensitic transformation from cubic L2_1 ordered austenite to NM martensite. As indicated by our DSC and magnetic measurements, there is no inter-martensitic transformation (IMT) in the Ga22-1 (x = 0) and Ga22-2 (x = 2) alloys. Therefore, HEXRD experiments were carried out only at 300 K and 100 K for the samples of Ga22-1 and Ga22-2, as shown in Figure 2a,b, respectively. All the reflection peaks can be indexed with the crystal structure of tetragonal non-modulated (NM) martensite. The corresponding lattice parameters are listed in Table 1. The results shown in Figure 2 confirm that there is indeed no IMT in these two alloys upon cooling to 100 K.

Table 1. Lattice parameters of Ga22-1 (x = 0) and Ga22-2 (x = 2) alloys at 300 K and 100 K.

| Alloy   | T (K) | a (Å)  | b (Å)  | c (Å)  |
|---------|-------|--------|--------|--------|
| Ga22-1  | 300   | 3.821  | 3.821  | 6.670  |
|         | 100   | 3.802  | 3.802  | 6.689  |
| Ga22-2  | 300   | 3.845  | 3.845  | 6.612  |
|         | 100   | 3.832  | 3.832  | 6.627  |

Figure 2. (a,b) High-energy X-ray diffraction patterns experimentally collected at 300 K and 100 K for the Ga22-1 (x = 0) alloy (a) and Ga22-2 (x = 2) alloy (b), respectively.

In situ HEXRD experiments were performed during cooling from 420 K to 100 K for the Ga22-3 (x = 4) alloy. Figure 3 shows the HEXRD patterns taken at 420 K, 350 K, and 100 K, respectively. At 420 K (Figure 3a), all the peaks can be well indexed according to the cubic L2_1 austenite structure. With the temperature decreasing to 350 K (Figure 3b), the Ga22-3 alloy transformed into 7M martensite (a_{7M} = 4.265 Å, b_{7M} = 5.512 Å, c_{7M} = 42.365 Å, β = 93.26°). On further cooling to 100 K (Figure 3c), the peaks characteristic of a modulated structure disappeared, and all the diffraction peaks can be well indexed according
to the NM martensitic structure, indicating that the sample had completely transformed into the NM martensite at this temperature. It can be concluded that the sequence of transformations in this Ga22-3 alloy is A→7M→NM during cooling, similar to the transformation sequence reported in an earlier study [25]. The temperature dependence of the lattice parameters of austenite and the two types of martensite is show in Figure 3d. The lattice parameters of 7M martensite only display a slight change because it exists in a narrow temperature region. In contrast, the lattice parameter $a_{NM}$ of the NM martensite decreases, while $c_{NM}$ increases obviously with decreasing temperature.

The typical HEXRD patterns collected during cooling from 380 K to 310 K across the Curie temperature (369 K) for the Ga22-4 ($x = 5.5$) alloy are shown in Figure 4. These patterns can be well indexed according to the cubic L2₃ austenite structure. There are no extra peaks besides those of the L2₃ austenite structure, which means that there is no second phase in this sample. In addition, when the sample was cooled from 380 K to 360 K, the HEXRD patterns did not show obvious changes in the peak profiles, which unambiguously confirms that there was no structural change associated with the Curie transition.
Figure 4. High-energy X-ray diffraction patterns collected during cooling from 380 K to 310 K for the Ga22-4 ($x = 5.5$) alloy.

Figure 5 shows the HEXRD patterns collected for the Ga22-4 ($x = 5.5$) alloy during cooling from 300 K to 160 K. At 300 K, most reflections can be indexed according to a five-layered modulated (5M) martensite structure using PowderCell software [26], as shown in Figure 5. This finding indicates that the martensitic transformation occurs between 310 K and 300 K. It should be noted that the main peak of (118)$_{5M}$ (Figure 5b) is very broad (Figure 5b). At the same time, the peaks of (-123)$_{5M}$ (Figure 5a) and (127)$_{5M}$ (Figure 5c) exhibit a striking asymmetry. These features clearly indicate that there is a tiny fraction of another martensite. Based on the evolution of the crystal structure upon further cooling (as shown below), we can initially confirm there is a small amount of seven-layered modulated (7M) martensite at this temperature. In fact, this 7M martensite structure was confirmed by TEM observation at room temperature (see Figure 7).

As shown by the evolution of the typical reflections (around (-123)$_{5M}$, (127)$_{5M}$ and the main peaks of 5M martensite) during cooling for the Ga22-4 ($x = 5.5$) alloy, although (-123)$_{5M}$ remained a singlet, this peak gradually broadened with decreasing temperature (Figure 5a). Furthermore, there is a minor peak at $2\theta = 3.36^\circ$ (around the (127)$_{5M}$ peak) (Figure 5c), which can be indexed as (12.13)$_{5M}$. It is interesting to note that, with decreasing temperature, the intensity of (12.13)$_{5M}$ gradually became stronger, while the (127)$_{5M}$ peak became weaker (Figure 5c). In addition to these small peaks, the evolution of the main peaks has been analysed, as shown in Figure 5b. At first, there is a small hump on the lower $2\theta$ side of (00.10)$_{5M}$, and then the hump evolves to a small peak at -230 K. On both sides of (125)$_{5M}$, two new peaks appear and develop during cooling. All these new peaks
can be well indexed according to the 7M martensite structure, as shown in Figure 5b. Thus, based on the above analyses, it can be concluded that the fraction of 7M martensite increased little by little during cooling, whereas the amount of 5M martensite gradually decreased.

The width of the (-123)\textsubscript{7M} peak was found to be very broad on further cooling below 150 K for the Ga22-4 (x = 5.5) alloy, as shown in Figure 6a. On the other hand, the intensity of (127)\textsubscript{7M} became similar to that of (12.13)\textsubscript{5M} at ~130 K (Figure 6c). When the temperature was further lowered to 120 K, the intensity of (12.13)\textsubscript{5M} surpassed that of (127)\textsubscript{7M}. Both the 5M and 7M martensites coexist upon cooling down to 100 K. Therefore, the 5M and 7M martensitic phases coexist over a wide temperature interval. Most importantly, the HEXRD pattern shows significant changes during cooling: the (112)\textsubscript{5M} peak of non-modulated martensite appears and develops at 2θ = 2.95° below 150 K (Figure 6b), whereas the (00.10)\textsubscript{7M} disappears. This finding indicates that there is a 5M → NM inter-martensitic transformation at temperature T1.

**Figure 6.** High-energy X-ray diffraction patterns around 2θ = 2.8° (a), 2θ = 3.0° (b), and 2θ = 3.4° (c) collected during cooling from 150 K to 100 K for the Ga22-4 (x = 5.5) alloy.

Thus, the evolution of the HEXRD profiles during cooling reveals that the Ga22-4 alloy undergoes a structural phase transition from the high-temperature cubic L2\textsubscript{1} austenite phase to the monoclinic martensitic phases (5M + 7M) between 310 K and 300 K, and the monoclinic 5M subsequently transforms to the tetragonal NM martensite at approximately 150 K. From 300 K to 160 K, 5M + 7M multiple martensites coexist, and the coexistence of 5M + 7M + NM multiple martensites is observed between 150 K and 100 K.

It is inferred from the above analyses that 5M and 7M martensitic phases coexist at room temperature for the Ga22-4 (x = 5.5) alloy. To further confirm these martensitic phases, a TEM experiment was conducted. Figure 7b shows a typical TEM bright-field image of stripe-like martensites in the Ga22-4 alloy. Two types of martensitic phases, which are interlocked, coexist. The corresponding selected area electron diffraction patterns (SAEDPs) of these two types of martensites, taken along the [111] zone axis of the austenitic phase, are displayed in Figure 7d,e, respectively. Our careful analysis shows that Figure 7d corresponds to 7M martensite, where six satellite spots are marked by blue arrows, and Figure 7e corresponds to 5M martensite, where four extra satellite spots between the main reflection are marked by blue arrows. The high-resolution transmission electron microscopy (HRTEM) images of 7M and 5M martensites are shown in Figure 7a,c, respectively. The images present contrast modulations with a period of 14 atomic layers [27] and a spacing c = 2.82 nm for 7M in Figure 7a, and a period of 10 atomic layers and a spacing c = 2.11 nm for 5M in Figure 7c. Therefore, the martensitic phase consists of a mixture of 5M and 7M structures, which agrees with the HEXRD results.
Figure 7. High resolution transmission electron microscopy (HRTEM) image of seven-layered modulated (7M) martensite for the Ga22-4 (x = 5.5) alloy at room temperature (a), TEM bright-field image (b), HRTEM image of five-layered modulated (5M) martensite (c), and the corresponding selected area electron diffraction patterns (SAEDPs) of 7M (d) and 5M (e) martensites.

The evolution of the HEXRD patterns for the Ga22-5 (x = 7) alloy was studied, and Figure 8a shows the HEXRD patterns collected at 350 K and 110 K. At 350 K, all the diffraction peaks can be well indexed according to the cubic L21 austenite structure, while, at 260 K, the diffraction pattern can be well indexed according to the 5M martensite structure (a_{5M} = 4.212 Å, b_{5M} = 5.592 Å, c_{5M} = 21.055 Å, β = 90.31°, see Figure 8b). With decreasing temperature, the HEXRD pattern shows no change even upon cooling to 110 K (a_{5M} = 4.221 Å, b_{5M} = 5.585 Å, c_{5M} = 20.998 Å, β = 90.35°), indicating that, besides the martensite transformation, there is no IMT. The HEXRD patterns and phase transformation sequence of the Ga22-6 (x = 8) alloy resemble those of Ga22-5, and the corresponding HEXRD patterns and lattice parameters are shown in Figure 9a,b, respectively.

Figure 8. High-energy X-ray diffraction patterns experimentally collected at 350 K and 110 K for the Ga22-5 (x = 7) alloy (a). The temperature dependence of the lattice parameters is shown in (b).
Based on the above results, the phase diagram of Ni$_{57-x}$Mn$_{21+x}$Ga$_{22}$ (x = 0, 2, 4, 5.5, 7, 8) was constructed and is shown in Figure 10. For x = 0 and 2, the martensite maintains the non-modulated (NM) structure even upon cooling to 100 K. For x = 4, with decreasing temperature to 350 K, the L2$_1$: austenite transforms into 7M martensite. On further cooling to 300 K, the sample shows the tetragonal NM martensite structure. Therefore, the sequence of transformation during cooling in this sample is A→7M→NM. For x = 5.5, the alloy undergoes a structural phase transition from the high-temperature cubic austenite phase (L2$_1$) to the monoclinic martensite phases (5M + 7M) at approximately 300 K and subsequently from the monoclinic martensite phase to the tetragonal martensite phase at approximately 150 K. From 300 to 160 K, multiple martensites 5M + 7M coexist, and the coexistence of multiple martensites 5M + 7M + NM is observed between 150 K and 100 K. For x = 7 and 8, the cubic L2$_1$: austenite transforms into 5M martensite, which remains stable down to 100 K.
3.3. Magnetic-Field-Triggered Transition between Coexisting Multiple Martensites

To probe the possible transformation between coexisting multiple martensites of the Ga22-x (x = 5.5) alloy under magnetic fields, we performed in situ neutron diffraction experiments with an increasing magnetic field from 0 T to 6 T at 140 K. The results are shown in Figure 11a. The 5M, 7M and NM martensites indeed coexist at 140 K, which is consistent with the HEXRD results. To trace the structure evolution of the 5M, 7M and NM martensites, the intensities of typical peaks of coexisting multiple martensites as a function of applied magnetic field are displayed in Figure 11b. With the increasing magnetic field, the intensity of (110)NM shows an increasing trend, whereas the intensity of (10.10)7M shows a decreasing trend, and the intensity of (-105)5M shows a negligible change. It could be inferred that a magnetic field as low as 0.2 T could trigger the transformation from 7M martensite to NM martensite.

![Figure 11](https://example.com/figure11.png)

**Figure 11.** HEXRD patterns at different magnetic field levels in the 2θ range from 30° to 140° for the Ga22-4 (x = 5.5) alloy (a). Evolution of HEXRD patterns as a function of applied magnetic field (b).

One possible reason for the magnetic-field-triggered transition from 7M martensite to NM martensite is as follows. In fact, when 5M, 7M and NM martensites coexist, these multiple martensite phases have similar free energy [28,29]. However, when an external field is applied, the free energy of these multiple martensites could become different. The transformation from 7M martensite to NM martensite may occur because, under the applied magnetic field, the free energy of NM martensite is lower than that of 7M martensite. In other words, the NM martensite is more stable under the magnetic field. It should be noted that, among the 5M, 7M and NM martensites, the NM martensite is also the most stable phase during cooling [25,30,31] or under applied stress [32]. Therefore, it is believed that the relative stability of the multiple martensites under the magnetic field and applied stress is related to their stability during cooling. The transformation between coexisting multiple martensites triggered by a low magnetic field may lead to novel magneto-responsive properties.

4. Conclusions

The crystal structure and phase transition as functions of the temperature and composition of Ni57−xMn21+5Ga22 (x = 0, 2, 4, 5.5, 7, 8) (at. %) magnetic shape memory alloys were systemically studied by a synchrotron X-ray diffraction technique. A phase diagram of this Ni57−xMn21+5Ga22 alloy system was constructed. With increasing x, the structure of martensite that is directly transformed from austenite evolves from the tetragonal NM structure to monoclinic 7M and 5M structures. The Ni53Mn26.5Ga22 (x = 5.5) alloy shows coexisting 5M + 7M multiple martensites in the temperature range from 300 K to 160 K and 5M + 7M + NM multiple martensites between 150 K and 100 K. The structural response of the
coexisting multiple martensites to the magnetic field in this Ni_{51.5}Mn_{26.5}Ga_{22} alloy was investigated by in situ neutron diffraction experiments. A magnetic field as low as 0.2 T could trigger the transformation from 7M martensite to NM martensite at 140 K in this alloy. This study is instructive for understanding the phase transition between coexisting multiple martensites under external fields and for designing novel functional properties based on such phase transitions.

**Author Contributions:** Conceptualization, L.H. and D.C.; methodology, M.W.; validation, L.H., D.C., M.W. and Y.W.; formal analysis, L.H.; investigation, L.H.; resources, D.C.; data curation, L.H.; writing—original draft preparation, L.H.; writing—review and editing, D.C.; supervision, D.C. and Y.W.; project administration, D.C.; funding acquisition, Y.W. All authors have read and agreed to the published version of the manuscript.

**Funding:** We acknowledge the support from the National Natural Science Foundation of China (Nos. 51701070, 51731005 and 51527801), Provincial Natural Science Foundation of Hunan (Grant No.2019JJ50101), the Scientific Research Fund of Hunan Province Education Department (Grant No.17A046, 14B042). Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Science, under Contract No. DE-AC02-06CH11357.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data presented in this article are available at request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Ulakkoo, K.; Huang, J.K.; Kantner, C.; O’Handley, R.C.; Kokorin, V.V. Large magnetic-field-induced strains in Ni2MnGa single crystals. *Appl. Phys. Lett.* **1996**, *69*, 1966.
2. Sozinov, A.; Likhachev, A.A.; Lanska, N.; Ulakkoo, K. Giant magnetic-field-induced strain in NiMnGa seven-layered martensitic phase. *Appl. Phys. Lett.* **2002**, *80*, 1746–1748, doi:10.1063/1.1458075.
3. Kainuma, R.; Imano, Y.; Ito, W.; Sutou, Y.; Morito, H.; Okamoto, S.; Kitakami, O.; Oikawa, K.; Fujita, A.; Kanomata, T.; et al. Magnetic-field-induced shape recovery by reverse phase transformation. *Nature* **2006**, *439*, 957–960, doi:10.1038/nature04493.
4. Karaca, H.E.; Karaman, I.; Basaran, B.; Ren, Y.; Chumlyakov, Y.I.; Maier, H.J. Magnetic Field-Induced Phase Transformation in NiMnCoIn Magnetic Shape-Memory Alloys—A New Actuation Mechanism with Large Work Output. *Adv. Funct. Mater.* **2009**, *19*, 983–998, doi:10.1002/adfm.200801322.
5. Krenke, T.; Duman, E.; Acet, M.; Wassermann, E.F.; Moya, X.; Mañosa, L.; Planes, A. Inverse magnetocaloric effect in ferromagnetic Ni-Mn-Sn alloys. *Nat. Mater.* **2005**, *4*, 450.
6. Huang, L.; Cong, D.; Suo, H.L.; Wang, Y.D. Giant magnetic refrigeration capacity near room temperature in Ni40Co10Mn40Sn10 multifunctional alloy. *Appl. Phys. Lett.* **2014**, *104*, 132407, doi:10.1063/1.4870771.
7. Sharma, V.; Chattopadhyay, M.K.; Shae, K.H.B.; Chouhan, A.; Roy, S.B. Large magnetoresistance in Ni50Mn34In16 alloy. *Appl. Phys. Lett.* **2006**, *89*, 222509, doi:10.1063/1.2399365.
8. Zhang, B.; Zhang, XX.; Yu, S.Y.; Chen, J.L.; Cao, Z.X.; Wu, G.H. Giant magnetothermocatalytic conductivity in the Ni–Mn–In ferromagnetic shape memory alloys. *Appl. Phys. Lett.* **2007**, *91*, 012510, doi:10.1063/1.2753710.
9. Ding, Z.; Liu, D.; Qi, Q.; Zhang, J.; Yao, Y.; Zhang, Y.; Cong, D.; Zhu, J. Multistep superelasticity of Ni-Mn-Ga and Ni-Mn-Ga-Co-Cu microwires under stress-temperature coupling. *Acta Mater.* **2017**, *140*, 326–336, doi:10.1016/j.actamat.2017.08.035.
10. Moya, X.; Kar-Narayan, S.; Mathur, N.D. Caloric materials near ferroic phase transitions. *Nat. Mater.* **2014**, *13*, 439–450, doi:10.1038/nmat3951.
11. Gottschall, T.; Skokov, K.; Burriel, R.; Gutleisch, O. On the S(T) diagram of magnetocaloric materials with first-order transition: Kinetic and cyclic effects of Heusler alloys. *Acta Mater.* **2016**, *107*, 1–8, doi:10.1016/j.actamat.2016.01.052.
12. Smith, A.; Bahl, C.R.; Bjork, R.; Engelbrecht, K.; Nielsen, K.K.; Fryds, N. Materials Challenges for High Performance Magnetocaloric Refrigeration Devices. *Adv. Energy Mater.* **2012**, *2*, 1288–1318, doi:10.1002/aenm.201200167.
13. Wang, Y.; Huang, E-W.; Ren, Y.; Nie, Z.; Wang, G.; Liu, Y.; Deng, J.; Choo, H.; Liaw, P.; Brown, D.; et al. In situ high-energy X-ray studies of magnetic-field-induced phase transition in a ferromagnetic shape memory Ni–Co–Mn–In alloy. *Acta Mater.* **2008**, *56*, 913–923, doi:10.1016/j.actamat.2007.10.045.
14. Yang, S.; Bao, H.; Zhou, C.; Wang, Y.; Ren, X.; Matsushita, Y.; Katsuya, Y.; Tanaka, M.; Kobayashi, K.; Song, X.; et al. Large Magnetostriiction from Morphotrophic Phase Boundary in Ferromagnets. *Phys. Rev. Lett.* **2010**, *104*, 197201, doi:10.1103/physrevlett.104.197201.
15. Ahart, M.; Somayazulu, M.; Cohen, R.E.; Ganesh, P.; Dera, P.; Mao, H.-K.; Hemley, R.J.; Ren, Y.; Liermann, H.-P.; Wu, Z. Origin of morphotropic phase boundaries in ferroelectrics. Nature 2008, 451, 545–548, doi:10.1038/nature06459.

16. Bergstrom, R.; Wuttig, M.; Cullen, J.; Zavalij, P.; Biber, R.; Dennis, C.; Garlea, V.O.; Laver, M. Morphotropic Phase Boundaries in Ferromagnets: Tb17Dy6Fe2 Alloys. Phys. Rev. Lett. 2013, 111, 017203, doi:10.1103/physrevlett.111.017203.

17. Murray, S.J.; Marioni, M.; Allen, S.M.; O’Handley, R.C.; Lograsso, T.A. 6% magnetic-field-induced strain by twin-boundary motion in ferromagnetic Ni–Mn–Ga. Appl. Phys. Lett. 2000, 77, 886.

18. Nie, Z.; Liu, D.M.; Wang, G.; Ren, Y.; Wang, Y.D.; Brown, D.E.; Zuo, L. Strain-induced dimensionality crossover and associated pseudoelasticity in the martensitic phase of Ni2MnGa. Appl. Phys. Lett. 2010, 97, 171905, doi:10.1063/1.3506508.

19. Pons, J.; Chernenko, V.A.; Santamarta, R.; Cesari, E. Crystal structure of martensitic phases in Ni-Mn-Ga shape memory alloys. Acta Mater. 2000, 48, 3027.

20. Cong, D.Y.; Zetterström, P.; Wang, Y.D.; Delaplane, R.; Peng, R.L.; Zhao, X.; Zuo, L. Crystal structure and phase transformation in Ni49Mn28Ga23 shape memory alloy from 20 K to 473 K. Appl. Phys. Lett. 2005, 87, 111906, doi:10.1063/1.2043250.

21. Chernenko, V.A.; Villa, E.; Salazar, D.; Barandiaran, J.M. Large tensile superelasticity from intermartensitic transformations in Ni49Mn28Ga23 single cryocrystal. Appl. Phys. Lett. 2016, 108, 071903.

22. Studer, A.J.; Hagen, M.E.; Noakes, T.J. Wombat: The high-intensity powder diffractometer at the OPAL reactor. Phys. B: Condens. Matter 2006, 385–386, 1013–1015, doi:10.1016/j.physb.2006.05.323.

23. Takeuchi, I.; Famodu, O.; Read, J.; Aronova, M.; Chang, K.-S.; Craciunescu, C.; Lofland, S.; Wuttig, M.; Wellstood, F.; Knauss, L.; et al. Identification of novel compositions of ferromagnetic shape-memory alloys using composition spreads. Nat. Mater. 2003, 2, 180–184, doi:10.1038/nmat829.

24. Lanska, N.; derberg, O.S.; Sozinov, A.; Ge, Y.; Ullakko, K.; Lindroos, V.K. Composition and temperature dependence of the crystal structure of Ni–Mn–Ga alloys. J. Appl. Phys. 2004, 95, 8074.

25. Srivastava, S.K.; Srivastava, V.K.; Joshi, A.; Kamasa, P.; Varga, L.K.; Khovaylo, V.V.; Chatterjee, R. A low temperature anomaly observed in off-stoichiometric Ni-Mn-Ga system studied by higher harmonic ac-susceptibility measurements. Appl. Phys. Lett. 2010, 97, 122505.

26. Kraus, W.; Nolze, G. POWDER CELL—A program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. J. Appl. Crystallogr. 1996, 29, 301.

27. Zheng, H.; Wang, W.; Xue, S.; Zhai, Q.; Frenzel, J.; Luo, Z. Composition-dependent crystal structure and martensitic transformation in Heusler Ni–Mn–Sn alloys. Acta Mater. 2013, 61, 4648–4656, doi:10.1016/j.actamat.2013.04.035.

28. Ke, X.Q.; Wang, D.; Ren, X.; Wang, Y. Formation of monoclinic nanodomains at the morphotropic phase boundary of ferroelectric systems. Phys. Rev. B 2013, 88, 214105, doi:10.1103/physrevb.88.214105.

29. Jin, Y.M.; Wang, Y.U.; Khachatryan, A.G.; Li, J.F.; Viehland, D. Conformal Miniaturization of Domains with Low Domain-Wall Energy: Monoclinic Ferroelectric States near the Morphotropic Phase Boundaries. Phys. Rev. Lett. 2003, 91, 197601, doi:10.1103/physrevlett.91.197601.

30. Pagounis, E.; Chulist, R.; Lippmann, T.; Laufenberg, M.J.; Skrotzki, W. Structural modification and twinning stress reduction in a high-temperature Ni-Mn-Ga magnetic shape memory alloy. Appl. Phys. Lett. 2013, 103, 111911, doi:10.1063/1.4819335.

31. Chernenko, V.A.; Segui, C.; Cesari, E.; Pons, J.; Kokorin, V.V. Sequence of martensitic transformations in Ni-Mn-Ga alloys. Phys. Rev. B 1998, 57, 2659.

32. Huang, L.; Cong, D.Y.; Wang, Z.L.; Nie, Z.H.; Dong, Y.H.; Ren, Y.; Zhang, Y.; Wang, Y.D. Direct evidence for stress-induced transformation between coexisting multiple martensites in a Ni–Mn–Ga multifunctional alloy. J. Phys. D Appl. Phys. 2015, 48, 265304.