Intermartensitic transformation and magnetic-field-induced strain in $Ni_{52}Mn_{24.5}Ga_{23.5}$ single crystals

W. H. Wang, G. H. Wu,[a] J. L. Chen, S. X. Gao, and W. S. Zhan
State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

G. H. Wen and X. X. Zhang
Department of Physics, The Hong Kong University of Science and Technology Clear Water Bay, Kowloon, Hong Kong, People's Republic of China

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We have found a complete thermoelastic intermartensitic transformation between modulated and unmodulated martensite in single-crystal $Ni_{52}Mn_{24.5}Ga_{23.5}$. This intermartensitic transformation provides a much larger strain than that of the martensitic transformation. A giant switching-like strain of ±5.0% can be achieved by a small magnetic field of 0.2 T upon the intermartensitic transformation. In the modulated martensite, a large recoverable magnetic-field-induced strain of up to 1.2% has been obtained. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1396820]

$Ni_{50}Mn_{25}Ga_{25}$ with cubic L21 structure[1] is a ferromagnetic Heusler alloy possessing a thermoelastic martensitic phase transition. This material exhibits a shape-memory effect upon the martensitic transformation and a magnetic-field-induced strain (MFIS)[2–6] in martensite. There has been strong interest in this material for potential applications as magnetic-field-controlled actuator material. In addition to the martensitic transformation, an intermartensitic transformation also exists, which is the focus of this work. The intermartensitic transformation is a first order phase transition between the modulated (*M type*) and the unmodulated (*T type*) martensite at lower temperature.[7–9] Previously, the observed intermartensitic transformation revealed a nonthermoelastic behavior[7] and appeared only in prestressed samples.[8,9] In this letter, we report the observation of a complete thermoelastic intermartensitic transformation in single crystals of $Ni_{52}Mn_{24.5}Ga_{23.5}$. The occurrence of this transformation has been attributed to the metastable state of the modulated martensite. We have found that the intermartensitic transformation provides a much larger strain than that of the martensitic transformation. Similar to the case of martensitic transformation, the strain upon the intermartensitic transformation can also be controlled by an external magnetic field. Quantitatively, we have obtained a switching-like shape memory effect of 5.0% achieved by applying a magnetic field of only 0.2 T and a large MFIS up to 1.2% in an unloaded sample.

Single crystals of $Ni_{52}Mn_{24.5}Ga_{23.5}$ were grown by the Czochralski method as reported previously.[10] The magnetization was measured with a superconducting quantum interference device (SQUID, Quantum Design MPMS) magnetometer. The strain was measured along the [001] direction using a metal strain gauge with magnetic fields up to 1.5 T applied along the [001] and [100] directions.

Figure 1 shows the temperature dependence of the magnetization in a magnetic field of 0.1 mT for a single crystal $Ni_{52}Mn_{24.5}Ga_{23.5}$. The martensite start temperature M_S and the reverse transformation start temperature A_S are 285 and 289 K, respectively. There is another distinct structural transformation, namely, the *intermartensitic transformation*, occurring at T_I=205 K during cooling and reverse at T_R=240 K during heating with a temperature hysteresis of 35 K. Clearly, our observed intermartensitic transformation shows a *complete* thermoelastic behavior. This is in sharp contrast to earlier observation. The intermartensitic transformation has been observed previously in some prestressed samples[8,9] and in some samples richer in Mn.[7] However, the previously observed transformation is *nonthermoelastic*, that is, the transformation between *M* and *T* type could only be generated either during cooling or during heating. What is unique in our sample is that the $M-T$ transformation can be ob-

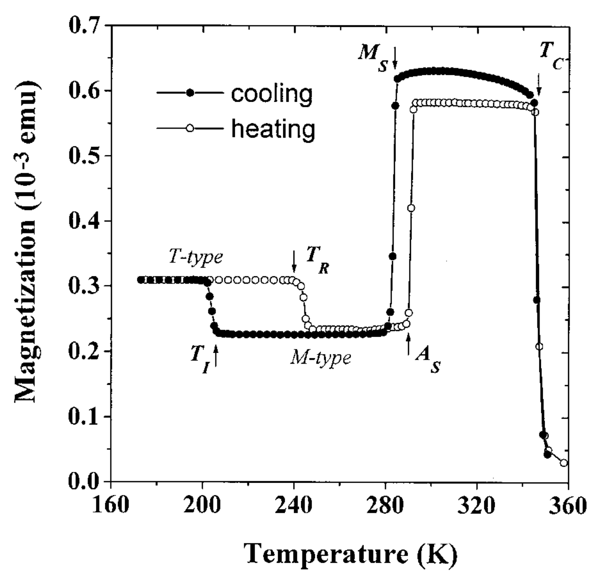

FIG. 1. Temperature dependence of the magnetization for $Ni_{52}Mn_{24.5}Ga_{23.5}$ single crystal. The Curie temperature T_C, the martensite start and reverse transformation start temperature M_S and A_S, and the intermartensite start and reverse transformation start temperature T_I and T_R, as marked by the arrows, respectively.

[a]Electronic mail: userm201@aphy.iphy.ac.cn

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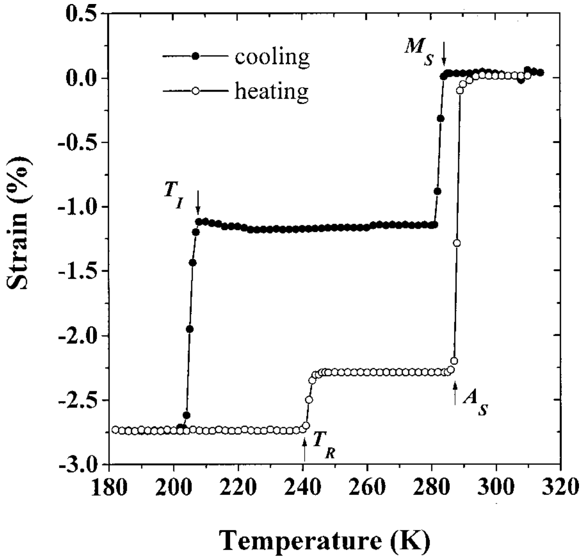

FIG. 2. Strain as a function of temperature measured in [001] direction during cooling and heating processes without the bias field.

tained unequivocally at specific temperatures during both cooling and heating. The mechanism of the complete thermoelastic behavior will be detailed in a future publication.

Figure 2 shows the strain along the [001] direction as a function of temperature in the same single crystals. During cooling from the room temperature, the sample contracts about 1.2% through the martensite transformation at M_S. Further cooling through the intermartensitic transformation at T_I, brings about another contraction of 1.5%. Such a large strain has not been observed previously. During heating, through the reverse intermartensitic and the reverse martensitic transformation, the deformation of the sample is entirely recovered. It is similar to the two-way shape memory behavior observed on Ti-50.2 (at. %) Ni alloy.[11]

The deformation strain can be strongly affected by a magnetic field. Figure 3 shows the strain as a function of temperature under a biasing magnetic field of 0.2 T applied perpendicularly to the intrinsic strain direction. While the

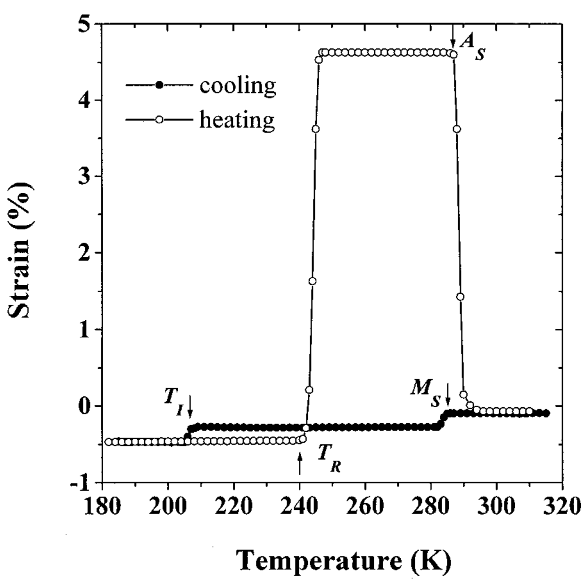

FIG. 3. Strain as a function of temperature measured in [001] direction with the bias field of 0.2 T applied along the [100] direction.

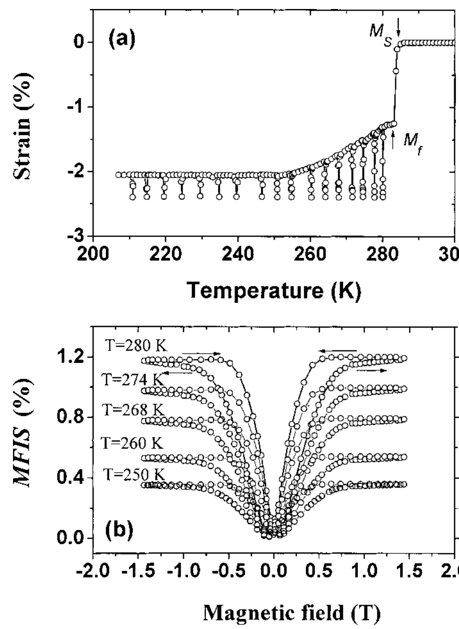

FIG. 4. (a) Strain as a function of temperature measured in [001] direction during cooling. After the sample was cooled down to 280 K, a magnetic field was applied to the sample along the strain-measuring direction from 0 to 1.5 T and then back to zero at a temperature interval of 2 K; (b) MFIS as a function of magnetic field at the different temperatures.

field suppresses the strain through the two transformations during cooling, it substantially enhances the strain during the two reverse transformations upon heating. A very large expansion of 5% and contraction of −5% have been observed through the reverse intermartensitic transformation at T_R and the reverse martensitic transformation at A_S.

The effect of magnetic field is to cause a preferential orientation of the martensitic variants, leading to a shape deformation of the sample.[10] The shape-memory behavior shown in Fig. 3 can be attributed to a competition between the effect of the magnetic field and the intrinsic strain of the sample. The applied field perpendicular to the intrinsic strain direction tends to suppress the intrinsic strain. As shown in Fig. 3, a small field of 0.2 T makes such suppression nearly complete (only −0.1% and −0.15% upon the two transformations). Therefore, the elastic deformation energy generated by two transformations was stored in a self-accommodation state by the martensite. Upon the two reversed transformations during heating, a dramatic situation occurs. The effect of field superposes on the intrinsic strain, leading to a substantial enhancement of the shape deformation as large as 5.0%. The strain is even larger than the sum of two subsequent strains in the absence of field (see Fig. 2). Thus, the magnetic field works as an energy valve to release deformation energy upon the reverse intermartensitic transformation. Further heating through the reverse martensitic transformation recovers the deformation and brings the sample to its parent phase.

The modulated martensite is a metastable phase with many mobile twin boundaries. By driving the twin boundary motion using a magnetic field, it is possible to obtain a large MFIS. Figure 4(a) shows the strain in [001] direction as a function of the temperature during cooling. After the sample was cooled down to 280 K (below the martensite finish temperature M_f point of 282 K) without the magnetic field, we applied a magnetic field of up to 1.5 T along the [001] direction then back to zero and measured the MFIS at a temperature interval of 2 K. The maximum MFIS shown in Fig. 4(a) was 1.2% at $T=280$ K. This is the largest recoverable MFIS ever reported from an unloaded sample. In comparison, the magnitude of magnetostriction is 0.2% at saturation for Terfenol-D, which currently is the best magnetostrictive solid. As seen in Fig. 4(a), the MFIS decreases as temperature is lowered, reflecting the decrease of the mobility of the martensitic variants and the variation of the elastic property of the material. It should be noted that the MFIS became a constant of 0.35% in the temperature range between 250 and 202 K. It implies that the magnetic field always has the same set of twin boundaries moving around.

Figure 4(b) shows the relationship between the MFIS and the applied magnetic field at different temperatures (280, 274, 268, 260, and 250 K). In Ni–Mn–Ga alloys, the process of saturation of the MFIS has been predicted governed by both the elastic energy and the magnetic anisotropy energy.[12] At all temperatures, however, the saturated fields for MFIS are the same at about 0.8 T, which is consistent with the saturated field for magnetization.[13] This observation indicates that approach to saturation of MFIS is mainly dominated by the magnetic anisotropy energy in *M-type* intermartensite. Reducing the uniaxial magnetic anisotropy will be an effective means to reduce the saturated field for MFIS.

In summary, we have found a complete thermoelastic behavior in the intermartensitic transformation in single crystal $Ni_{52}Mn_{24.5}Ga_{23.5}$. This transformation generates a larger shape deformation of 1.5%. Utilizing a low magnetic field of only 0.2 T, the elastic energy generated by both of martensitic and intermartensitic transformation can be stored during cooling and released at the reverse intermartensitic transformation. The burst of elastic energy creates a switching-like giant strain of 5.0% during heating. We have also found that, in the metastable modulated martensite, a recoverable large MFIS of 1.2% can be achieved at a saturated field of 0.8 T.

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