

## Characteristics of 5M modulated martensite in Ni-Mn-Ga magnetic shape memory alloys

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The applicability of the magnetic shape memory effect in Ni-Mn-based martensitic Heusler alloys is closely related to the nature of the crystallographically modulated martensite phase in these materials. We study the properties of modulated phases as a function of temperature and composition in three magnetic shape memory alloys  $\text{Ni}_{49.8}\text{Mn}_{25.0}\text{Ga}_{25.2}$ ,  $\text{Ni}_{49.8}\text{Mn}_{27.1}\text{Ga}_{23.1}$  and  $\text{Ni}_{49.5}\text{Mn}_{28.6}\text{Ga}_{21.9}$ . The effect of substituting Ga for Mn leads to an anisotropic expansion of the lattice, where the  $b$ -parameter of the 5M modulated structure increases and the  $a$  and  $c$ -parameters decrease with increasing Ga concentration. The modulation vector is found to be both temperature and composition dependent. The size of the modulation vector corresponds to an incommensurate structure for  $\text{Ni}_{49.8}\text{Mn}_{25.0}\text{Ga}_{25.2}$  at all temperatures. For the other samples the modulation is incommensurate at low temperatures but reaches a commensurate value of  $q \approx 0.400$  close to room temperature. The results show that commensurateness of the 5M modulated structure is a special case of incommensurate 5M at a particular temperature. © 2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4932233>]

Currently, Ni-Mn-based Heusler alloys are intensively investigated for their multifunctional properties such as magnetic shape-memory (MSM), magneto-caloric effect (MCE), and giant magneto-resistance (GMR) making them interesting materials for technological applications.<sup>1</sup> These effects rely on the presence of a magnetostructural martensitic transition, the temperature which can be controlled by alloying, strain, and to a certain extent, by an external magnetic field.<sup>2</sup> The characterization and detailed knowledge of the properties of magneto-structural transitions of these materials is vital for the correct choice of the temperature ranges of their usage. Especially, the MSM property of these materials is closely related to the martensite structure. Magnetic field induced strain (MFIS), which is basically the magnetic shape memory property, is observed in modulated martensite phases, and the magnitude of the MFIS differs depending to the modulation. While MFIS is 6% for the 5M modulated martensite,<sup>3</sup> it is 10% for 7M modulated martensite.<sup>4</sup> Besides this, recent studies have shown that MFIS can be also observed in non-modulated  $L1_0$  tetragonal martensite reaching about 12% for a Ni-Co-Cu-Mn-Ga alloy.<sup>5</sup> This indicates that the occurrence of MSM is not necessarily related to the modulation, but instead to twin boundary mobility. A martensite structure with high twin boundary mobility, and hence high MFIS, exhibits low twinning stress,  $\sigma_{TW}$ . The twinning stress increases with decreasing temperature.<sup>6</sup> Studies on this property have shown that twinning stress is closely related to the structural parameters, and it is possible to decrease  $\sigma_{TW}$  by letting  $c/a \rightarrow 1$ .<sup>5,7</sup>

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Additionally, our recent studies have shown that due to the presence of intermartensitic transitions at low temperatures, the initial martensite state occurring just below the transition temperature is not stable for some compositions of Ni-Mn-Ga and Ni-Mn-Sn alloys.<sup>8,9</sup> Particularly for Ni-Mn-Ga alloys, intermartensitic transitions exhibit a broad thermal hysteresis. The occurrence of intermartensitic transitions also places limits on the useful temperature range of the usage of magnetic shape-memory materials. The broad hysteresis effect has to be taken into account in variable temperature environments so that the material can be used with desired capacity in MSM applications.

In view of these properties, it is important to understand the structural parameters and their temperature and compositional dependencies for alloys showing MSM behavior. Near-room-temperature magnetic shape-memory effect in  $\text{Ni}_{50}\text{Mn}_{50-x}\text{Ga}_x$  occurs roughly in the range  $21 \leq x \leq 24$ . At these compositions, the martensite structure is modulated tetragonal. Although the modulation is often referred to as 5M or 7M, depending on the composition, more recent studies have shown that the modulation is in general incommensurate (IC), and even more, that the designation 5M(IC) or 7M(IC) is just a measure of the modulation vector length; and that a specific designation may not even be needed.<sup>10,11</sup> Moreover,  $q$  can also be temperature-dependent and can carry the structure from commensurate to incommensurate modulations of various extensions such as 5-fold or 7-fold.

In this work, we study the temperature and concentration dependence of the crystallographic parameters including the modulation vector of 5M modulated martensite in  $\text{Ni}_{49.8}\text{Mn}_{25.0}\text{Ga}_{25.2}$  ( $x = 25.2$ ),  $\text{Ni}_{49.8}\text{Mn}_{27.1}\text{Ga}_{23.1}$  ( $x = 23.1$ ), and  $\text{Ni}_{49.5}\text{Mn}_{28.6}\text{Ga}_{21.9}$  ( $x = 21.9$ ) alloys. The sample with  $x = 25.2$  transforms from a high-temperature austenite phase to a low temperature modulated martensite phase and remains in this state to the lowest temperatures. The sample with  $x = 23.1$  also transforms similarly, but an additional  $L1_0$  phase appears at lower temperatures. The sample with  $x = 21.9$  exhibits martensite structure with the mixture of 5M and 7M martensite, as well as an  $L1_0$  mixture at lower temperatures.<sup>8</sup>

The samples were prepared by arc melting high purity elements and were annealed under Ar at 1073 K in sealed quartz tubes for 5 days. The compositions were determined by energy dispersive x-ray analysis using a scanning electron microscope. X-ray measurements were carried out on a conventional source using Cu K-alpha radiation and using the ID22 spectrometer at the ESRF, Grenoble. The measurements were carried out in the temperature range  $10 \leq T \leq 300$  K.

To study the nature of the 5M martensite state, we have performed x-ray diffraction studies on  $\text{Ni}_{50}\text{Mn}_{25-x}\text{Ga}_x$  alloys in the concentration range  $25 \leq x \leq 21$ . Structural refinements were based on the superspace approach for orthorhombic and monoclinic modulated structures of Ni-Mn-Ga alloys.<sup>12,13</sup>

The temperature dependence of the lattice parameters  $a$ ,  $b$ , and  $c$  in the 5M state for three samples are given in figs. 1(a)-1(c), up to their respective martensite transition temperatures. For all three samples,  $b$  increases with increasing temperature, the  $c$ -parameter is practically temperature-independent, and  $a$  shows a weak decrease with increasing temperature. The irregularities in the data for  $x = 21.9$  are due to the fact that the lattice parameters have to be extracted among coexisting 7M and nonmodulated  $L1_0$  phases.

Fig. 1(d) shows the temperature dependence of the unit cell volume. The cell volume is defined as the volume reduced to the primitive tetragonal cell and is calculated as  $a \times \sqrt{2}b \times c$ . The volume increases with increasing temperature so that the thermal expansion properties are similar. One further sees that at all temperatures, the volume decreases with increasing  $x$ , i.e., with increasing Ga concentration. As an example, the overall composition dependence of the volume at 10 K is shown in fig. 2(a). The fact that Ga with an atomic radius 1.35 Å is larger than that of Mn with 1.27 Å can at first thought to be the underlying reason for this behavior. However, a plot of the lattice parameters as a function of composition at 10 K in fig. 2(b) shows that the lattice does not expand isotropically with increasing Ga concentration, but rather the  $b$ -parameter increases while the  $a$  and  $c$  parameters decrease. This shows that the size of the atomic radii of the individual atomic species is not sufficient to explain the compositional dependence of the lattice parameters. Rather, the nature of this anisotropic variation has to be related to the differences in the binding forces in the three major crystallographic directions with changing composition.

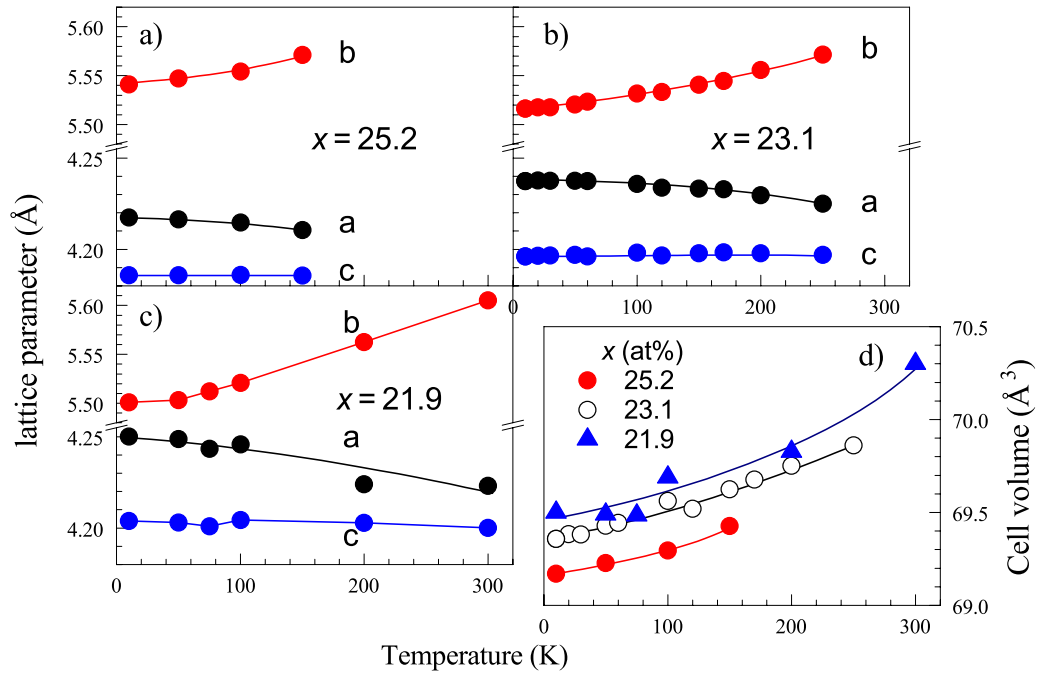


FIG. 1. Temperature dependence of lattice parameters. a)  $x = 21.9$ , b)  $x = 23.1$ , and c)  $x = 25.2$ . d) The temperature dependence of the unit cell volume for the three samples.

In fig. 3, we compare the temperature variation of the modulation vector  $q(T)$  and the tetragonality  $c/a$  relative to the primitive cell. Here  $c \rightarrow \sqrt{2}b$  and  $a \rightarrow (a + c)/2$ .  $q(T)$  is shown in fig. 3(a). For  $x = 25.2$  and  $x = 23.1$ ,  $q(T)$  shows a weak decrease with similar slopes with increasing temperature for both samples. At low temperatures,  $q \approx 0.43$  for  $x = 25.2$  indicating an incommensurate configuration that remains as such up to the stability limit of the martensite phase. This result is in good agreement with those obtained earlier.<sup>14</sup> For  $x = 23.1$ ,  $q \approx 0.41$  at low temperatures, also indicating incommensuratness, but tends to a commensurate 5M configuration with  $q = (2/5) = 0.4$ .

$q(T)$  for the  $x = 21.9$  sample shows a more rapid variation with temperature than that of the samples discussed above. In fact, to further verify the validity of this data we have measured a second sample with a similar composition,  $x = 21.4$ . For these two samples  $q(T)$  shows similar behavior. Close to room temperature  $q \approx 0.40$  showing commensuratness. However, an incommensurate modulation with  $q \approx 0.40$  develops rapidly with decreasing temperature. The development of 7M and  $L1_0$  in the structure, coexisting with 5M, can cause strain which can lead to the more rapid change in  $q(T)$  than for the former two samples which are purely 5M down to the lowest temperatures. In all cases,  $q$  increases with decreasing temperature as does the twinning stress.

As seen in fig. 3(b),  $c/a$  not only decreases with decreasing temperature but also with decreasing Ga concentration, particularly at low temperatures. Therefore, as the tetragonality increases, i.e. as  $c/a$  decreases, the modulation vector increases. It would be interesting to relate the twinning stress and twin mobility to the  $q$ -vector to gain more insight into the material properties of MSM alloys in terms of their crystallography. It is already known that the twinning stress increases with decreasing temperature, and therewith the twin boundary mobility decreases. Since  $q$  increases with decreasing temperature, it remains to be understood how the increase in  $q$  can be related to increased twinning stress. One reasoning can be provided by taking into account the local strains caused by the incommensuratness itself. The incommensurate 5M modulated state corresponding to  $q > 0.40$  is a state in which particular strains can appear since these large unit cells are connected with irregular locations of the atoms bounding the unit cell, and this situation carries over long distances. Only in the case when the modulation becomes commensurate are the atoms at the boundaries of the unit cell located at equivalent positions from cell to cell. This configuration would be expected to carry the least strain. Therefore, an increase in  $q$  from the commensurate

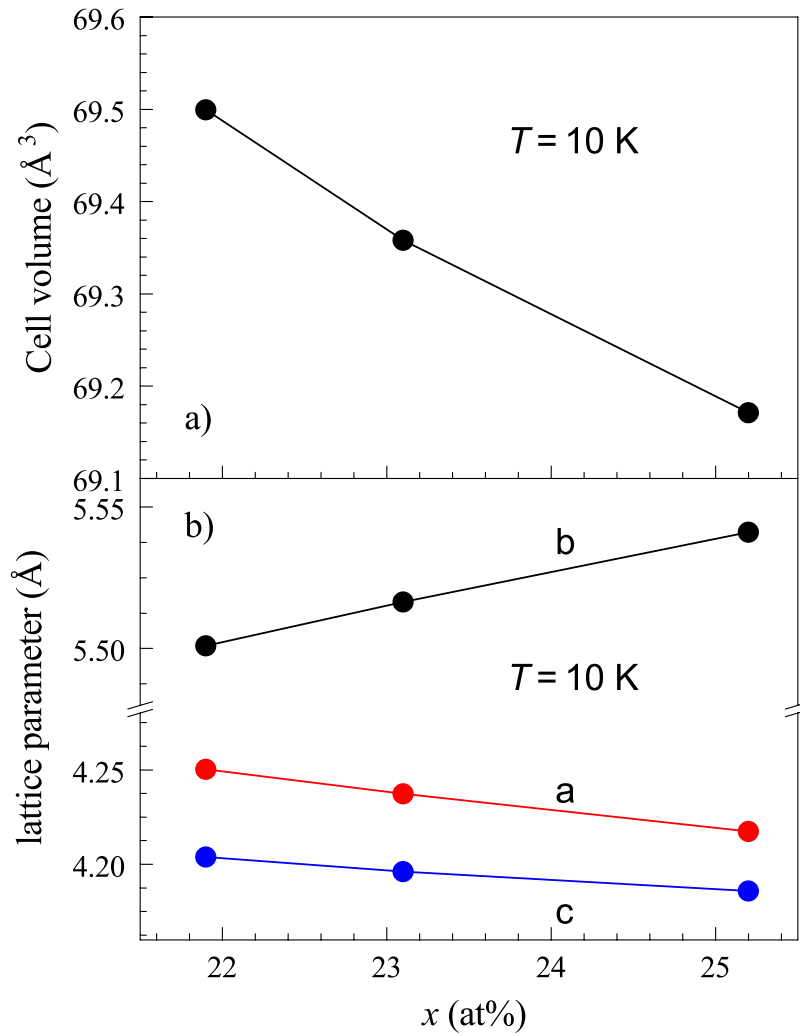


FIG. 2. Compositional dependence of structural parameters at 10 K. a) cell volume and b) lattice parameters.

case of  $q = 0.40$  would cause an increase in twinning stress and a decrease in twin mobility due to increased strain. However, this point requires further investigations to be conclusive.

As long as 5M is the only form of martensite present in the compound as in the case of  $x = 25.2$  and  $x = 23.1$ ,  $q$  decreases with increasing Mn composition as evidenced in fig. 3(a). With the argument given above, the decrease in Mn composition should then lead to a higher twin mobility. This behavior is, however, interrupted when 5M is not the only modulation present in the sample. 7M and  $L1_0$  appear in  $x = 21.9$  and  $x = 21.4$  as mentioned above, and the modulated 5M destabilizes faster with  $q$  changing more rapidly with temperature. The appearance of strain due to accommodating more than one type of structure could be causing this behavior.

We have carried out a study on the temperature and composition dependence of the crystallographic parameters in 5M martensite in  $\text{Ni}_{50}\text{Mn}_{25-x}\text{Ga}_x$ . The results reveal that replacing Ga by Mn leads to an anisotropic change in the lattice parameters so that a simple picture of adding an atom of smaller radius in place of a larger to cause an isotropic expansion does not hold. We also find that the modulation decreases with increasing temperature at similar rates in the compounds that remain in the pure 5M state throughout the martensite stability range. The rate of decrease with increasing temperature in  $q$  becomes smaller at Mn-richer compositions where admixtures of 7M and  $L1_0$  are introduced into the structure. More detailed studies are required on the structural properties of compositions that are richer in Mn to be able to gain information on the evolution of the commensurateness in these systems.

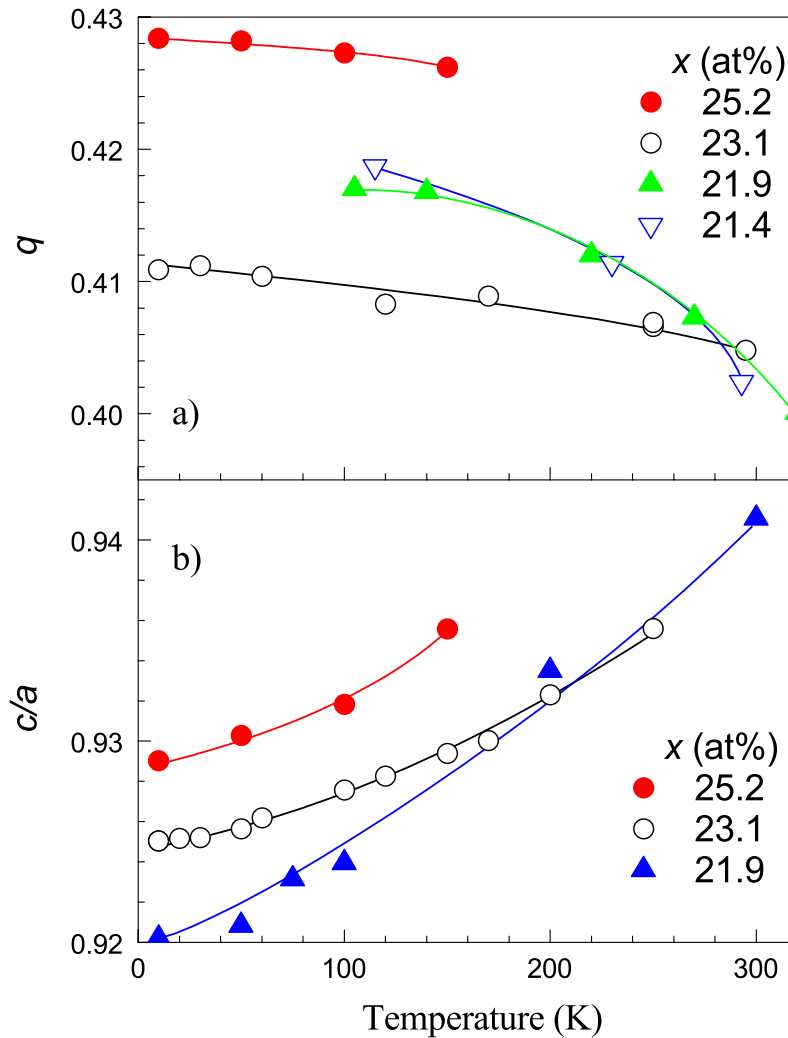


FIG. 3. Temperature dependence of the modulation vector for the investigated samples.

## ACKNOWLEDGMENTS

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