CRYSTAL STRUCTURES OF Ni$_2$MnGa FROM DENSITY FUNCTIONAL CALCULATIONS

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(Received ...)

Abstract

The different crystal structures of ferromagnetic Ni$_2$MnGa have been calculated using density functional theory (DFT) with special emphasis on the modulated structures 10M and 14M. These are important for understanding the stability of Ni$_2$MnGa martensites and their functionality as shape-memory materials. The modulated structures have been optimized in the calculations and their properties are discussed in relation to the structures without modulation. The occurrence of the modulated structures is related to the soft TA$_2$ phonon mode observed in Ni$_2$MnGa. The latter is related to the specific nesting behavior of the Fermi surface in Ni$_2$MnGa. Particular shapes of the modulated structures are stabilized by the covalent interaction mediated by the p-orbitals of Ga and d-orbitals of Ni. The role of this interaction becomes clear seen when considering the phonon dispersion spectrum of Ni$_2$MnGa, where some characteristic anomalies occur in the coupling of acoustical vibrational modes and the optical modes of Ni.

Keywords: Heusler alloys, Modulated structures, Density functional calculations

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1. INTRODUCTION

A hundred years have passed since the martensites had been discovered. However, during these days new martensitic structures are being discovered and special focus is now on the details of the microscopic nature of this phenomenon. This is due to the unique dynamical properties of martensitic structures, which are essentially different from other materials. This property is based on the mobility of the martensitic domains which allows to induce large macroscopic deformations of the sample by applying an external stress. This deformation does not cost much energy since the crystal structure remains unchanged; only the domain walls move. In turn, the high temperature austenitic structure does not show these structural domains. Therefore, heating up the system allows to get rid of the deformations supplied by the martensitic state. Whatever was done to the sample at lower temperatures will be forgotten at higher temperatures. Latter, one can cool down the sample to the martensitic state and apply new deformations knowing that everything can be removed as soon as the sample is heated up to the austenitic state. This is the essence of the shape-memory behavior which is a completely material dependent property and therefore requires significant knowledge of the crystals.

The technological importance of magnetic shape-memory materials (MSM) based on Ni$_2$MnGa has been discovered just a few years ago [17]. The idea here is to use an external magnetic field in order to induce the motion of martensitic twin boundaries, instead of pressure as in the non-magnetic martensites. This is possible because of ferromagnetic order of the martensite structure. In addition, this requires that the energy of magnetic anisotropy must be larger than the energy necessary for twin motion. These conditions are met in Ni$_2$MnGa, but to be more precise, in its off-stoichiometric compounds. It has been shown that one can achieve macroscopic deformations of about several percent in the sample by applying moderate magnetic fields and this can be used to design novel technological devices like actuators [1].

As mentioned above, the MSM effect is a material property. Depending on the kind of martensite formed at working temperatures the corresponding effect may be observed. Thus, about 6% strain was obtained in Ni-Mn-Ga [14]. The crystal structure of that martensite (10M) was defined as a tetragonal one ($a = b \neq c, \ c/a = 0.94$) with superposed five-layered modulation. This modulation is known as a kind of shuffling of the atoms which has a shape of a static wave propagating along the [110] direction [12, 22]. This wave has a polarization vector along [110], i.e., the shuffling is in-plane. The value of 6% has been predicted as maximum value for the 10M structure. Recently, new achievements have been reported where 10% magnetic-field-induced strains were obtained in Ni-Mn-Ga [18]. In this case the martensite was found to be the 7M (14M) structure which has an orthorhombic symmetry with superposed 7-layer modulation. It has even been argued that another martensitic
structure (T) of Ni-Mn-Ga could produce a strain up to 20%. This specific structure has tetragonal symmetry \((a = b \neq c, \ c/a \approx 1.25)\) without any modulation. However, this effect has not been observed so far and most probably the non-modulated structure T will not show that kind of MSM behavior. The lattice parameters of all these structures are listed in Table.

Each of the three structures, 5M (10M), 7M (14M) and T, can be the ground state depending on the composition of the alloy. Applying stress to the sample one can induce structural transformations between the 10M, 14M and T structures [12].

A microscopic explanation of the modulated structures is complicated. The presence of modulation can be seen from electron diffraction images where a number of additional spots appear between the main spots defined by the non-modulated structure. The number of additional spots allows to define how many atomic planes form a complete period of modulation. However, a pattern of atomic displacements cannot be defined uniquely in this way. Whenever some modulated structure is proposed it is a fit of the measured data to some model. Thus, the 10M structure was reported to have a wave-like pattern of the shuffling and the stability of such structure was confirmed by recent \textit{ab-initio} calculations [12, 22]. However, another model formed by long-order stacking sequences (instead of the wave-like distortions) can be used (this time for Ni-Mn-Al which is very similar to Ni-Mn-Ga) to explain the diffraction patterns with additional spots [13]. The latter form of the 10M structure has not been calculated so far, but most probably it will also be stable. Thus the idea here is not to decide which model is correct and which is wrong, but to presume that the modulation can be of two kinds: Wave-like or the stacking-like. Which modulation is finally realized in the sample may also depend on macroscopic strain fields which are present in the martensitic phase.

In case of the 14M structure the same ambiguity exists concerning the way how atoms move to form the modulation. Similar to the 10M (5M) structure, the 7-layered martensite also can be presented by the stacking-like modulation [13]. But completely different displacements of atoms were obtained from recent high-resolution neutron powder diffraction measurements [3]. The modulation in this case is wave-like but with a very complicated superposition of waves having different periods. Again it would be productive for further work to assume that both structures are to some extent correct.

In this work we report results of \textit{ab-initio} calculations for Ni\textsubscript{2}MnGa in its 7-layer martensite which is formed by the long-range stacking sequences as it was proposed for the case of Ni-Mn-Al [13]. The wave-like martensite is not considered in this work but left for future calculations.

Before discussing details of this work it is necessary to remember that Ni\textsubscript{2}MnGa is ferromagnetic system at room temperature \((T_C \approx 380 \text{ K})\) and undergoes a martensitic phase transformation (MT) at around 200 K [19].
Table 1: The martensitic structures of Ni-Mn-Ga and corresponding chemical compositions collected from Ref. [7]. The notations 10M and 14M stand for the 5-layered and 7-layered modulated structures. Depending on how the layers are defined (unit cells or distances between the atomic (110)-planes) these structures can be referred to as 5M and 7M, respectively. In all cases M means modulation. More details and how these martensitic structures can be transformed to each other can be found in Ref. [12].

| Lattice parameters (Å) | 5M (10M) | 7M (14M) | T  |
|------------------------|----------|----------|----|
| a                      | 5.90     | 6.12     | 6.44 |
| b                      | 5.90     | 5.78     | 5.52 |
| c                      | 5.54     | 5.54     | 5.52 |
| c/a                    | 0.94     | -        | ≈ 1.2 |
| Alloy                   | Ni1.95Mn1.23Ga0.81 | Ni2.02Mn1.17Ga0.80 | Ni2.10Mn1.08Ga0.84 |

The initial structure, known as the Heusler structure L2₁, has cubic symmetry. The magnetic moments are mainly localized on the Mn atoms ($\mu_{\text{tot}} = 4.09 \mu_B$, $\mu_{\text{Ni}} = 0.37 \mu_B$, $\mu_{\text{Mn}} = 3.36 \mu_B$, $\mu_{\text{Ga}} = -0.04 \mu_B$) [2]. A precursor phase transition occurs close to 260 K [24] and gives rise to a modulated super-structure 3M which is cubic in average but has some additional shuffling as calculated recently by Ayuela in Ref. [21]. The precursor phase transition shows prominent anomalies in phonon dispersions, magnetization and conductivity [24, 11, 6]. Below the martensitic transformation temperature ($T_M \approx 202$ K), Ni$_2$MnGa can be stable in different structures, with or without modulation, having tetragonal or orthorhombic symmetry as listed in Tab. 1. The structural transformations between the martensitic structures can be induced by external pressure.

The *ab-initio* total-energy calculations worked well for most of the structures of Ni$_2$MnGa [2]. The earlier calculations allowed to obtain two structures which do not possess any modulation shuffling of the atoms. These are the initial cubic structure L2₁ and a tetragonal martensitic structure with $c/a \geq 1.2$ [23]. All other structures show a shuffling of the atoms which cannot be explained by taking into account the short-range interactions alone. Allowing for shuffling of the atoms implies that calculations have to be done on relatively large supercells which is computationally very demanding. In case of the 10M structure a supercell of 40 atoms had to be simulated which can still be handled by the density functional method with sufficient accuracy [22]. The wave-like modulation 10M was calculated and found to be related to specific phonon properties of Ni$_2$MnGa as well as Fermi-surface nesting [21, 18, 10, 3]. In case of the 7M (14M) structure one would need to do calculations for a supercell containing 56 atoms. This has been carried out in the present work in order to define exact structural properties and
the criteria of stability of possible stacking-like 7M (14M) modulations (from now on we use the 14M notation only).

2. STRUCTURAL RELAXATIONS

In order to simulate the 14M structure, we used a supercell, which resembles the 7-layered structure proposed for Ni-Mn-Al alloys [13]. The supercell consists of seven tetragonal unit cells of Ni$_2$MnGa. This allows us to incorporate the full period of the 14M stacking sequences in the supercell. The (110) atomic planes are shifted along the [110] direction so that the modulation propagates along [110]. Altogether we use 14 atomic planes perpendicular to [110] in order to form the supercell. By this construction, two full 7-layered periods fit into the supercell but also one may choose different variants of stackings to be simulated. The initial stacking shifts were chosen to satisfy the angle $\gamma \approx 3.5^\circ$ known for the monoclinic 14M supercell of Ni-Mn-Al [13]. This makes the shift of two consecutive planes with respect to each other to be 0.3 Å.

The Vienna Ab-initio Simulation Package (VASP) [8, 9] has been used to perform the electronic structure calculations. The projector-augmented wave formalism (PAW), implemented in this package, [3, 9] leads to very accurate results compared to all-electron methods. Within density-functional theory, the electronic exchange and correlation are treated by using the generalized gradient approximation [15]; the 3$d$ electrons of Ga have been included as valence electrons. The Monkhorst-Pack k-points generation scheme was used with a grid of $10 \times 8 \times 2$ points in the full Brillouin zone of the whole supercell.

The structural relaxation was performed with respect to the ionic positions, the shape and the volume of the supercell. We have considered two possible choices of long-period stacking order sequences: A “right” one (52$\bar{2}$) and a “wrong” one (535$\bar{T}$). The 535$\bar{T}$ structure is different from the normal 14M structure in the sense that it has an unusual stacking sequence for modulated structures. We have simulated this specific structure in order to see whether this modulation can be stabilized. The resulting 14M$_{535\bar{T}}$ structure is shown schematically in Fig. 1(a). The relaxation has led to a slightly different shape and volume but the “wrong” initially supplied shape remained unchanged. We suppose that this means not only the “wrong” stacking corresponds to a local energy minimum but that there can be other structures of this kind. The structure shown in Fig. 1(a) has a monoclinic symmetry ($a \neq b \neq c$, $\alpha = \beta = 90^\circ \neq \gamma$) with the structural parameters: $a_{535\bar{T}} = 4.26$ Å, $b_{535\bar{T}} = 29.32$ Å, $c_{535\bar{T}} = 5.43$ Å, $\gamma = 86^\circ$. The basal planes are shifted with respect to each other by about 0.34 Å.

Another structure (14M$_{(5\bar{2})}_2$) which has been optimized is shown in Fig.
This structure is the one which usually is considered as the 14M stacking-like structure. We note that this structure has also almost remained unchanged during the relaxation. It appears as if any king of stacking could be stabilized. However, all possible variants might have different energies which eventually defines their relative stability. We compare the total energies of the calculated stacking structures with the energies which we already know for other structures of Ni$_2$MnGa. Figure 2 shows how the relative total energies of different structures depend on the $c/a$ ratio which defines the tetragonality of the structure. The zero energy corresponds to the cubic L2$_1$ structure. One of the curves was calculated for a simple unit cell of Ni$_2$MnGa with 4 atoms which shows two energy minima corresponding to the cubic high-temperature L2$_1$ ($c/a = 1$) structure and the tetragonal non-modulated martensite T ($c/a \approx 1.25$). The T structure has a lower energy compared to the cubic structure as is expected for the zero temperature calculations. Another curve with just one minimum of energy was calculated with a supercell of 40 atoms which had a superposed and optimized wave-like 5-layered modulation [22]. The minimum at $c/a = 0.94$ corresponds to the 10M structure which is however metastable with respect to the T structure. We could not perform $c/a$ calculations for the discussed in this work stacking-like structures because of the computational costs, but the energies of this structures are shown in Fig. 2. One can see that even the “wrong” stacking leads to a lower energy compared to the cubic structure. But the “right” 14M structure turns out to be more stable. Thus, we conclude that even though different stacking sequences can be realized, they differ in total energy.

Finally we show in Fig. 3 the total energy surface projected onto the plane ($b/a$, $c/a$), where $a$, $b$ and $c$ are the lattice parameters of the conventional Heusler structure [19]. The iso-energy contour lines show minima corresponding to the cubic L2$_1$ structure ($b/a = 1$, $c/a = 1$) and the tetragonal T structure. This energy surface was calculated for a small unit cell containing 4 atoms and therefore shows no minima corresponding to the modulated structures. But since we are now able to calculate all modulated structures of Ni$_2$MnGa, it is possible to show the positions of the minima which would appear if the modulations were taken into account.

3. CONCLUSIONS

We have performed total energy DFT calculations in order to simulate the 14M structure of Ni$_2$MnGa. Initially we assumed that the modulation of this structure is stacking-like in contrast to the wave-like one. The latter modulation was earlier found to coincide with the 10M structure. Here we show that the stacking makes the 14M structure stable. However, we found that the stacking sequence is not unique. Different choices of the stacking
order may be made, which however leads to different total energies. The fact that the structure prefers stacking instead of having a perfect structure agrees with our previous investigations. It has already been discussed elsewhere that the system likes to break the local symmetry which facilitates the formation of hybrid states of \( p \)-orbitals of Ga [20]. This changes the distribution of the spin-down electronic density of states right at the Fermi level and lowers the total energy. The role of phonon softening in relation to the modulation has still to be understood. By having the 14M structure simulated we have completed the list of structures found for Ni\(_2\)MnGa experimentally (Tab. 1). Now all these structures have been obtained by DFT calculations. In further work we will simulate the wave-like 14M structure. Another point to note is that the relative energies of the simulated structures may be different in experiment since the martensitic structures of Ni-Mn-Ga are compositionally dependent. The martensitic domain structure may also favor some of the structures while all the calculations are done for a single martensite variant.

Acknowledgments

Financial support by the German Science Council (Graduate College “Structure and Dynamics of Heterogeneous Systems”) and by the SFB-491 is very much acknowledged.

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Figure 1:
The modulated stacking-like 14M structures of Ni$_2$MnGa simulated in this work. The black, gray and white circles show the Ni, Mn and Ga atoms, respectively. The directions are shown according to the conventional cubic Heusler structure of Ni$_2$MnGa [19]. (a) The 14M$_{5351}$ structure (the “wrong” 14M). (b) The 14M$_{(55)}_{2}$ structure (the “right” 14M).

Figure 2:
The relative total energies of different structures of Ni$_2$MnGa versus the c/a ratio, which defines the tetragonal distortion of the lattice. The zero energy corresponds to the energy of the cubic L2$_1$ structure. The 14M structures are shown here to have lower energies compared to the L2$_1$ structure. The 14M$_{(55)}_{2}$ modulation is more stable than the 14M$_{5351}$ one.

Figure 3:
The total energy surface with iso-energy contour lines plotted to show the energy minima which can be obtained without taking the modulations into account. If the modulations are simulated the energy surface would have additional minima corresponding to the 10M and 14M structures. However it is impossible to obtain all minima on one (b/a,c/a) plane because if a modulation is superposed on the structure, the T structure disappears (see Fig. 2). Also the 10M and 14M modulations have different periods and characters of shuffling.
Figure 1: A. Zayak, W. A. Adeagbo, P. Entel and V. D. Buchelnikov
Figure 2: A. Zayak, W. A. Adeagbo, P. Entel and V. D. Buchelnikov
Figure 3: A. Zayak, W. A. Adeagbo, P. Entel and V. D. Buchelnikov