Role of shuffles and atomic disorder in Ni-Mn-Ga

A. T. Zaya and P. Entel
Institute of Physics, University Duisburg-Essen, 47048 Duisburg, Germany
(Dated: July 11, 2018)

We report results of ab-initio calculations of the ferromagnetic Heusler alloy Ni-Mn-Ga. Particular emphasis is placed on the stability of the low temperature tetragonal structure with $c/a = 0.94$. This structure cannot be derived from the parent $L2_1$ structure by a simple homogeneous strain associated with the soft elastic constant $C'_1$. In order to stabilise the tetragonal phase, one has to take into account shuffles of atoms, which form a wave-like pattern of atomic displacements with a well defined period (modulation). While the modulation is related to the soft acoustic $[110]$-TA$_2$ phonon mode observed in Ni$_2$MnGa, we obtain additional atomic shuffles, which are related to acoustic-optical coupling of the phonons in Ni$_2$MnGa. In addition, we have simulated an off-stoichiometric systems, in which $25\%$ of Mn atoms are replaced by Ni. The energy of this structure also exhibits a local minimum at $c/a = 0.94$. This allows us to conclude that both shuffles and atomic disorder stabilize the $c/a = 0.94$ structure. In both cases the stability seems to be associated with a dip in the minority-spin density of states (DOS) at the Fermi level, being related to the formation of hybrid states of Ni-$d$ and Ga-$p$ minority-spin orbitals.

Keywords: Ni-Mn-Ga alloys, martensitic phase, modulated structure

(Ni-Mn-Ga alloys (close to stoichiometric Ni$_2$MnGa) are known to exhibit unique magneto-elastic properties. They are ferromagnetic at room temperature ($T_C \sim 380\, K$), and undergo (including the precursor) a two-step martensitic transformation for $T_M < T_C$ ($T_M \sim 200\, K$) [1]. In the martensitic state of Ni-Mn-Ga the structure consists of differently oriented martensitic domains (twin variants), which are also magnetic domains. This makes the martensitic structure of Ni-Mn-Ga sensible to an external magnetic field, which can induce a redistribution of the martensitic domains in the sample. Those domains with easy magnetic axes are along the field will gain in energy on cost of the domains with less favourable orientation of the magnetisation. Alignment of twin variants by the motion of twin boundaries can result in large macroscopic strain up to $6\%$ [2, 3].

This effect is used in the magnetic-shape-memory (MSM) technology [4]. The MSM technology is based on the magnetic field induced redistribution of martensitic domains in the sample. From a technological point of view, Ni-Mn-Ga is more promising than other materials being presently in commercial use, for example, the well-known material Tb-Dy-Fe (Terfenol-D) which exhibits magnetostrictive strains of about $0.1\%$. Design of new efficient MSM magneto-mechanical actuator devices is in progress [5].

In this work we discuss the stability of different structures inside a single martensitic variant of Ni-Mn-Ga. From experimental studies we know that these alloys can form at least three different phases in the martensitic state [6]. Depending mostly on composition, crystals can be found in the modulated tetragonal structure with $c/a = 0.94$ known as $5M$ or $10M$, the orthorhombic modulated structure $7M$, or the tetragonal structure with $c/a \approx 1.2$. Sometimes, the modulated structures are also denoted by $5R$ and $7R$ [7].

The central question concerns the nature of the modulation in the $5M$ and $7M$ structures, which has often not been taken into account in theoretical investigations [8-10]. However, the modulation plays a basic role in Ni$_2$MnGa, as shown by recent first-principles calculations [11]. In the literature, it is argued that the reason for the modulation arises from specific nesting properties of the Fermi surface in Ni$_2$MnGa, which in turn, causes softening of the acoustic $[110]$-TA$_2$ phonon mode [12].

In the previous study [11] of the stability of the $5M$ structure, we have drawn attention to specific changes in the DOS, namely a dip, which develops in the minority-spin density of states (DOS) at the Fermi level, being related to the Fermi surface geometry [13]. Analysis of the partial contributions to the DOS shows that this dip is formed by Ni-$d_{\downarrow}$ and Ga-$p_{\downarrow}$ electrons. Hence, there is a strong evidence that the formation of alike hybrid states might contribute to the stability of the modulated structures. In addition to the shuffles leading to the modulation, atomic disorder and non-collinearity of magnetic moments were proposed as possible factors being also responsible for the structural stability of the modulated phases in Ni-Mn-Ga.

In this work, we discuss properties of the modulated $5M$ structure with new features which have been obtained in recent calculations. In addition, we consider an off-stoichiometric composition of Ni-Mn-Ga with excess Ni replacing Mn atoms. For the total energy calculation we use the Vienna Ab-initio Simulation Package (VASP) [14,15] and the implemented projector-augmented wave formalism (PAW) [16]. The electronic exchange and correlations are treated by the generalised gradient approx-
supercell. Actually, all parameters of the calculations are points in the full Brillouin zone for the long orthorhombic the Monkhorst-Pack method with a grid of $10 \times 2 \times 8$ points in the full Brillouin zone for the long orthorhombic supercell. Actually, all parameters of the calculations are

![Diagram of modulated martensitic structure of Ni$_2$MnGa (5M)](image)

**FIG. 1:** Modulated martensitic structure of Ni$_2$MnGa (5M) shown schematically: (a) projection of the 5M structure on the (001) plane (top view) and (b) projection of the 5M structure on the (110) plane (side view). Filled, open and gray dots show the positions of Mn, Ni and Ga, respectively. In addition to the modulation, which moves the atoms along the [110] direction only, there is a tiny shuffling of the atoms of the order of 0.001 Å (≈ 1% of the modulation amplitude), which moves the atoms in [001] and [110] directions. The extremely small displacements of atoms have been enlarged in the figure for clarity.

In order to simulate the 5M structure, we used a supercell, which resembles the five-layered structure obtained by V. V. Martynov and V. V. Kokorin in experiment [6]. The supercell consists of five tetragonal unit cells of Ni$_2$MnGa, similar to those used in Ref. [9]. This allows us to incorporate the full period of the 5M modulation in the supercell [11]. The basal plane is spanned by [110] and [001] of the L2$_1$ structure with the modulation along [110]. Altogether we use ten atomic planes perpendicular to [110] in order to form the supercell. The modulation is generated by displacing these atomic planes along [110] direction. By this construction, two full five-layered periods fit into the supercell. The initial magnitudes of the atomic displacements were chosen according to the 5M structure of Ref. [11], for the Ni-plane equal to 0.324 Å and for the Ga-Mn-plane equal to 0.292 Å.

This supercell has an orthorhombic symmetry with lattice parameters $a \approx 4.17$ Å, $b \approx 20.73$ Å, $c \approx 5.633$ Å, yielding a tetragonality ratio of $c/a \approx 0.955$, i.e., we take exactly the structure which was obtained theoretically in Ref. [11]. In the calculations we allowed for relaxation of the structure by changes of the volume, cell shape and atomic positions. The plane-wave cutoff energy was equal to 241.6 eV and the k-points were generated using the Monkhorst-Pack method with a grid of $10 \times 2 \times 8$ points in the full Brillouin zone for the long orthorhombic supercell. Actually, all parameters of the calculations are

![Diagram of off-stoichiometric supercell of Ni$_2$+xMn$_{1-x}$Ga](image)

**FIG. 2:** Off-stoichiometric supercell of Ni$_2$+xMn$_{1-x}$Ga for $x \approx 0.25$ created by replacing Mn by an Ni atom in one of the 16 positions of the L2$_1$ structure.

The structure obtained after relaxation is shown in Fig. 1a and b. As in the model for the 5M structure in Ref. [6,11], the modulation has form of a static wave with polarization (the direction in which the atoms move) along [110], which is perpendicular to the propagation direction [110]. All atoms move with the same phase that agrees with the acoustic mode [12,17]. However, a careful analysis shows that the shuffling of the atoms in Ni$_2$MnGa consists of two different contributions, being a superposition of them. The first one is the modulation which is wave-like. While the second one is different in the sense that it is not a wave. We call these additional shuffles tetrahedral distortions, similar to those considered by Harrison for tetrahedrally coordinated solids having the symmetry of diamond or zincblende [18]. According to Harrison, radial and angular distortions of tetrahedral structures stand for this motion of the atoms. In case of Ni$_2$MnGa each Ni atom is surrounded by two tetrahedrals formed by Ga and Mn, respectively. Note that amplitudes of the tetrahedral distortions are of the order of 0.001 Å which is ≈1% of the modulation amplitude.

We would like to draw attention to some features related to the tetrahedral distortions. In the (001) plane, Fig. 1a, the Ga and Ni atoms move closer to each other, while the Mn atoms move towards the free space left by the Ni atoms. Also, the plane (110) in Fig. 1(b) shows couples of Ni atoms moving closer to their nearest Ga atom, while the nearest to them Mn atom is pushed out. Thus, each atom of Ga tends to couple with two Ni atoms, which will contribute to the hybridization of the Ga-$p$ and Ni-$d$ orbitals as discussed above. We stress that the modulation and the tetrahedral distortions must be considered separately from each other. The first one is related to the soft acoustic [110]-TA$_2$ phonon mode, while the second one is connected with the coupling of
The modulation facilitates the formation of hybrid Ga-
structures. In order to simulate an off-stoichiometric
composition, a cubic supercell of 16 atoms is used in the
calculations. The corresponding structure with a com-
position formula Ni$_{8+1}$Mn$_{4-1}$Ga$_4$ is shown in Fig. 2.
An extra atom of Ni is placed into a Mn position (cen-
tral atom in Fig. 2). The supercell has been optimized,
first, with respect to the atomic positions and the vol-
ume. The $c/a = 1$ ratio was kept constant at this stage
of the calculations. After the relaxation, the optimal
volume became smaller (192.51 Å$^3$) compared to the sto-
ichiometric structure (195.79 Å$^3$) by about 1.6%. The
atomic positions have changed as well, but only for the
Ni atoms. The positions of Mn, Ga and the extra-Ni
remained unchanged, which is not physical, but is due
to the choice of the supercell and the periodic boundary
conditions used for the calculations. One would need to
simulate a bigger supercell for a more sophisticated treatment
of the defects in Ni-Mn-Ga. In Fig. 2 the extra-Ni is
shown in the center connected by bonds to its eight
nearest Ni neighbours. The relaxation has led to consid-
erable displacements of all eight Ni atoms towards the
extra-Ni along the bonds, while the rest of the structure
remains unchanged. The magnetic moments remained
ferromagnetically aligned. Although, the extra-Ni has
got a smaller magnetic moment (0.24 $\mu_B$) compared to
the regular Ni atoms ($\approx 0.35\ \mu_B$).

This relaxed cubic structure is now used to study the
impact of a tetragonal deformation. Fig. 3 shows the de-
pendence of the total energy on the $c/a$ ratio for the three
cases: the perfect stoichiometric Ni$_2$MnGa structure, the
5M structure, and the off-stoichiometric structure defined
by Ni$_{8+1}$Mn$_{4-1}$Ga$_4$. It turns out that the total energy
curve for the case of the off-stoichiometry has a minimum
at $c/a = 0.94$, exactly the value as for the 5M structure,
and in the experimental investigations. This shows that
both modulation and disorder are responsible for the sta-
ble tetragonal structure with $c/a = 0.94$.

Fig. 4 presents the total electronic density of states
for the off-stoichiometric case (structure shown in Fig.
2). The DOS is shown for: the cubic structure with
$c/a = 1$ and the tetragonal structure with $c/a = 0.94$.
Important is here the dip in the minority-spin density of
states right at the Fermi level. The dip is present for
both cases, but stronger developed for the more stable
tetragonal structure. The analysis of the partial DOS
shows again that the two peaks, responsible for the dip,
originate from the Ni-$d$ and Ga-$p$ orbitals (the effect is
similar to the results obtained for the 5M structure in Ref. [11]).

In summary, we have presented computational results
for the modulated 5M structure of Ni$_2$MnGa. We find that shuffles in Ni$_2$MnGa involve two different ef-
fects, which contribute to the pattern of the atomic dis-
placements. The first and the stronger contribution,
called modulation, arises from the soft acoustic [110]-TA$_2$
phonon mode, which is observed in the phonon spectrum
of Ni$_2$MnGa. The second effect, referred in our work as
tetrahedral distortions, yields small (as compared to the
modulation) atomic displacements and results from the
coupling between the acoustic [110]-TA$_1$ and LA with
corresponding low-energy optical modes of Ni. The cal-
culations for the off-stoichiometric Ni$_{8+1}$Mn$_{4-1}$Ga$_4$
supercell yield a local minimum of the total energy at
$c/a = 0.94$, which is the “natural” tetragonality ratio for
the Ni-Mn-Ga at low temperatures. The same tetragon-
ality ratio can be obtained in the calculations when
taking modulation (5M structure) into account. Simi-
lar to the case of the 5M structure, the stability of the

\[ E_{10} = \begin{bmatrix} 3 & 5 \\ 2 & 4 \end{bmatrix} \]

\[ E_{20} = \begin{bmatrix} 3 & 5 \\ 2 & 4 \end{bmatrix} \]
c/a = 0.94 ratio is related to a dip in the minority-spin electron density of states which develops from hybridizing Ni-d and Ga-p states right at the Fermi level, stabilizing the tetragonal variant with c/a = 0.94. In other words, the tetragonal structure becomes stable due to the covalent interaction of Ni an Ga atoms via the p-d hybrid electronic orbitals, the importance of which for the Heusler alloys have been discussed by Kübler et al. [19]. But we emphasize the role of the local symmetry loss which facilitates the formation of the p-d hybrid states. In future work we will perform calculations using the GGA+U method. This will split apart the bonding and anti-bonding states around the Fermi level, which will further deepen the dip discussed above. We expect that the resulting total energy will correspond then to the 5M structure as the ground state.

Acknowledgements

This work has been supported by the Graduate School “Structure and Dynamics of Heterogeneous Systems” of the Deutsche Forschungsgemeinschaft (DFG). We thank Dr. A. Postnikov, Dr. A. Ayuela and Dr. J. Enkovaara for valuable discussions.

References

[1] P. J. Webster, K. R. A. Ziebeck, S. L. Town, and M. S. Peak, Phil. Mag. 49 (1984) 295
[2] R.C. O’Handley, J. Appl. Phys. 83 (1998) 3263
[3] R. C. O’Handley, S. J. Murray, M. Marioni, H. Nembach, and S. M. Allen, J. Appl. Phys. 87 (2000) 4712
[4] K. Ullakko, J. K. Huang, C. Kantner, R. C. O’Handley, and V. V. Kokorin, Appl. Phys. Lett. 69 (1996) 1966
[5] I. Aaltio and K. Ullakko, Proceedings of the 7th International Conference on New Actuators, ACTUATOR 2000, Bremen Germany, June 2000, p.45
[6] V. V. Martynov and V. V. Kokorin, J. Phys. III (France) 2 (1992) 739
[7] Lluis Manosa, Antoni Planes, J. Zarestky, T. Lograsso, D.L. Schlagel and C. Stassis, Phys. Rev. B 64 (2001) 024305
[8] V. V. Godlevsky and K. M. Rabe, Phys. Rev. B 63 (2001) 134407
[9] A. Ayuela, J. Enkovaara, K. Ullakko, and R. M. Nieminen, J. Phys.: Condens. Matter 11 (1999) 2017
[10] A. T. Zayak, P. Entel, and J. Hafner, J. Phys.IV (France): International conference on martensitic transformations ICOMAT’02, 2003, to appear
[11] A. T. Zayak, P. Entel, J. Enkovaara, A. Ayuela, and R. M. Nieminen, J. Phys.: Condens. Matter 15 (2003) 159
[12] A. Zheludev, S. M. Shapiro, P. Wochner, and L. E. Tanner, Phys. Rev. B 54 (1996) 15045
[13] Yongbin Lee, Joo Yull Rhee, and B. N. Harmon, Phys. Rev. B 66 (2002) 054424
[14] G. Kresse and J. Furthmuller, Phys. Rev. B 54 (1996) 11169
[15] G. Kresse and D. Joubert, Phys. Rev. B 59 (1999) 1758
[16] Peter Blöchl, Phys. Rev. B 50 (1994) 17953
[17] A. T. Zayak, P. Entel, J. Enkovaara, A. Ayuela, and R. M. Nieminen, cond-mat/0304315 (2003)
[18] W. A. Harrison, Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond, W. H. Freeman and Company, San Francisco, 1980, pp. 185-192.
[19] J. Kübler, A. R. Williams, C. B. Sommers, Phys. Rev. B 28 (1983) 1745.

* Electronic address: alexei@thp.uni-duisburg.de