Ab initio calculations of structure and lattice dynamics in Ni-Mn-Al shape memory alloys

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Ab initio calculations of the magnetic shape-memory alloy Ni_{50}Mn_{x}Al_{50−x} with 0 ≤ x ≤ 50 were carried out using density functional theory and PAW potentials. The alloy is ferromagnetic in the range from 14 to 31 at.% Mn. The magnetic moment and structural properties are discussed in terms of the density of states.

Furthermore martensitic phases with long-periodic shuffling structure were calculated: 2M, 10M, and 14M. Their stability is discussed in respect to the electronic structure and the lattice dynamics, whereby phonon dispersion relations in [110] direction for the cubic L2₁ Heusler structure have been calculated. The transverse-acoustic phonon mode is shown to soften at the wave vector \(\mathbf{q}=\left[1/3 \ 1/3 \ 0\right]\) which confirms the tendency of Ni₂MnAl to form modulated structures at low temperatures. The theoretical results of the modulated martensitic phases correspond to experimental data, obtained from thin films near the stoichiometric composition.

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I. INTRODUCTION

Shape-memory (SM) alloys are of great interest from the technological point of view as sensor and actuator materials because of their inherent large strains and work capacity. While the SM effect is conventionally driven by temperature or applied stress, ferromagnetic (FM) SM-alloys provide the opportunity to drive a transformation of martensitic variants by an external magnetic field. These materials can be used where high switching frequencies are needed (e.g. in actuators) or where the necessary temperature changes are not applicable (e.g. in medical devices).

In this paper we present theoretical results of the (ferro)magnetic SM-alloy Ni-Mn-Al. This system belongs to the group of Heusler-alloys like the Ni-Mn-Ga alloy, being the most thoroughly investigated magnetic shape memory material to date, both theoretically (see, for example, Refs. 1–5) and experimentally (see, for example, Refs. 6–10). Recently, interest in the Ni-Mn-Al alloy system has grown, but only a few theoretical investigations of this alloy exist so far, mainly for the stoichiometric composition Ni₂MnAl. The advantage of Ni₂MnAl over Ni₂MnGa for technical applications is the higher ductility and the high martensite-austenite transition temperature of the Al containing alloy. However, in the Ni-Mn-Al system several modifications of martensite have been observed, which asks for a theoretical clarification in terms of their structural stability.

Therefore, in this study we investigate the structural and electronic properties of Ni_{50}Mn_{x}Al_{50−x} (with x ranging from 0 to 50 at.%) by ab initio calculations. Due to the constraints of the Heusler structure (L2₁, see Fig. 1), it is only applicable to vary the fraction of Mn and Al on their sublattice, while keeping the Ni sublattice unchanged in respect to the stoichiometric L2₁ structure. The magnetic moments, individual site occupation, and the spin density of states (DOS) are calculated for different compositions in this range.

In this class of alloys studied here, martensitic structures with long periodic modulations are of particular interest. Experimentally, various modulations with different stacking orders have been reported. For the theoretical investigation, here, the modulations 2M, 10M, and 14M, which are stable near the stoichiometric composition Ni₂MnAl, were chosen. The stability of these structures is examined in context with the density of states (DOS) and charge distribution between the atoms. X-ray diffractograms are simulated and compared with experi-
ment results.

Dynamical properties of the stoichiometric composition $\text{Ni}_2\text{MnAl}$ with the L$_2$1 cubic structure are studied within the supercell approach. Phonon dispersion relations are used to discuss the stability of $\text{Ni}_2\text{MnAl}$ at low temperatures and the role of modulation shuffles in this system. Elastic constants are derived from the slopes of the acoustic modes at the center of the Brillouin zone.

**II. COMPUTATIONAL DETAILS**

We used the Vienna *ab initio* simulation package $^{23}$ This package is a complex implementation of the density functional theory. Exchange and correlation energies are threaded by using the generalized gradient approximations by Perdew and Wang (PW91)$^{24}$.

Projector augmented wave functions $^{25,26}$ were used, which have proved to be superior to ultra-soft pseudo-potentials in describing magnetic compounds $^{23}$. The plane-wave cut-off energy is 337.4 eV for all calculations except for the long-periodic modulated phases 10M (323.9 eV) and 14M (202.4 eV). For all calculations a simple tetragonal (st) cell, shown in Fig. 2 was used. The lattice vectors of this cell $a'$, $b'$, and $c'$ are parallel to the $[\overline{1}10]$, [001], and [110] direction of the Heusler cell, respectively. The usage of a st cell makes the generation of off-stoichiometric and modulated structures more convenient. For larger cells $c'$ is increased. The k-point mesh is generated by the Monkhorst-Pack scheme with a grid of $8 \times 6 \times 8$ for the st cell, unless otherwise noted. (The number of subdivisions is decreased when increasing the cell size.) A smearing parameter of 0.2 eV is used. The magnetic moments are predefined by 1 $\mu_B$ on the Ni and Al atom sites and 3 $\mu_B$ on Mn the atom sites. Anti-ferromagnetic (AFM) structures are generated by alternating planes parallel to the (001) plane of up- and down-spin moments (see Fig. 2).

The phonon calculations were performed by using the force-constant method, whereby the Hellmann-Feynman forces have been computed in the elongated 1 st cell with 40 atoms. $^{27,28}$ The supercell was initially optimized so that all forces experienced by the atoms vanish. The force constants were calculated for $x$, $y$, and $z$ with individual displacements of the Ni, Mn, and Al atoms. The atoms have been displaced in both, positive and negative directions in order to obtain better accuracy of the forces. The displacement amplitudes were 30 pm. The plane-wave cutoff energy of 353.4 eV and a Monkhorst-Pack k-point generation scheme was used with a grid of $10 \times 8 \times 2$ points in the full Brillouin zone for the long supercell. The force constants were fitted to the Hellmann-Feynman forces by using the PHONON program $^{31}$. The values of the force constants decrease from the center of the supercell to its boundaries in [110] direction by several orders of magnitude which ensures accurate evaluation of the phonon dispersion.

**III. RESULTS AND DISCUSSION**

In section III A, we present the results of the *ab initio* calculations along with the physical properties derived for different alloy compositions. The stability and magnetic properties of these alloys are examined by the electronic structure and density of states in section III B. In section III C, we examine martensitic structures with long-periodic modulations. In section III D, we discuss the lattice dynamics of $\text{Ni}_2\text{MnAl}$ in view of the phonon dispersion relations evaluated for the cubic L2$_1$ structure in the ferromagnetic state. In section III E, we present elastic constants derived from phonon calculations.

**A. Structural data of $\text{Ni}_{50}\text{Mn}_x\text{Al}_{50-x}$**

Table I shows the lattice parameters and magnetic moments for the calculated $\text{Ni}_{50}\text{Mn}_x\text{Al}_{50-x}$ alloys with x ranging from 0 to 50 at.% in the FM and AFM structure. The calculated lattice parameter for $\text{Ni}_2\text{MnAl}$ is close to the experimental value of 0.5818 nm. $^{18}$ One can assume that the other lattice parameters also correspond to experimental values. We find that there is no significant variation in the volume of the cells by substituting Mn to Al (0.196 ± 0.003 nm$^3$). The small deviation from the expected cubic structure of $\text{Ni}_2\text{MnAl}$ is probably due to the unequally balanced k-point mesh. Calculations with a cubic cell prove this fact. An error of approximately 1 % in the c/a ratio is also expected for the other compositions. Only tetragonal distortions occurred by the relaxation of all degrees of freedom. A tetragonal structure with a c/a ratio well above 1.0 is more stable for alloys in the AFM state with high Mn concentrations only. This tetragonal structure can be explained by a Jahn-Teller effect: The system lowers its energy by a tetragonal distortion in the direction of c so that orbitals...
of neighboring Mn atoms of opposite spin overlap to a smaller extent.

By scanning over fixed volumes around the fully relaxed volume \( V_0 \) the bulk modulus of the compounds can be obtained. The volume-energy pairs are fitted with the Murnaghan equation\(^{27} \), that connects the energy \( E \) directly to the bulk modulus \( B \) and its pressure derivative \( B' \):

\[
E = E_0 + \frac{B_0 V}{B'(B'-1)} \left[ \left( \frac{V_0}{V} \right)^{B'} + B' \left( 1 - \frac{V_0}{V} \right) - 1 \right]. \tag{1}
\]

In Fig. 3 the energy depending on the cell volume is plotted for Ni\( _2 \)MnAl. The calculated values (crosses) correspond to the curve according to Murnaghan. The bulk moduli for some compositions are given in Table II together with other theoretical values. Furthermore, the cell is distorted uniaxial in the ground state volume. For scanning over different \( c/a \)-ratios a 16\( \times 12\times 16 \) k-point mesh was used. The energy relative to the ground state energy at the cubic structure versus the \( c/a \) ratio is given in Fig. 4. The slope of the curve flattens between \( c/a = 1.15 \) and 1.25, but no further local minimum in \( E(c/a) \) is found, unlike Ayuela et al.\(^{22} \) calculated with the FLAPW method. However, the tendency for a local minimum – found explicitly for Mn-rich compositions – is visible. Our results are converged in respect to the k-point mesh for the above given precision and basis set.

A tetragonal phase is only stable in AFM systems with high Mn concentrations like Table I reveals. Responsible for this fact could be an anti-bonding interaction between the \( d_{z^2} \) orbitals of neighboring Mn atoms. Through an expansion in \([001]\) direction these orbitals overlap less, which stabilizes a \( c/a \) ratio > 1.

To \( c/a \) ratios < 1 the energy rises steeply. However, structures with a \( c/a \) ratio < 1 are found experimentally. Additional deformations must therefore be responsible for the stabilization of these structures, e.g. modulations as discussed in part III C.

\[ \text{TABLE II: Bulk modulus } B_0 \text{ and its pressure derivative } B' \text{ for some compositions in the range Ni\textsubscript{50}Mn\textsubscript{x}Al\textsubscript{50-x}.} \]

\begin{center}

<table>
<thead>
<tr>
<th>System</th>
<th>( B_0 ) (GPa)</th>
<th>( B' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{50}Mn\textsubscript{57.5}Al\textsubscript{12.5} FM</td>
<td>169</td>
<td>11.78</td>
</tr>
<tr>
<td>Ni\textsubscript{50}Mn\textsubscript{53.3}Al\textsubscript{16.7} FM</td>
<td>125</td>
<td>3.57</td>
</tr>
<tr>
<td>Ni\textsubscript{2}MnAl FM</td>
<td>157</td>
<td>5.07</td>
</tr>
<tr>
<td>Ni\textsubscript{50}Mn\textsubscript{12.5}Al\textsubscript{37.5} FM</td>
<td>142</td>
<td>8.94</td>
</tr>
</tbody>
</table>

* theor., Ayuela et al., Ref. 22
\[ ^b \] theor., Godlevsky et al., Ref. 4

\begin{figure}[h]

\centering

\includegraphics[width=\textwidth]{fig3}

\caption{Energy change relative to the ground state energy \( E_0 = -25.172 \text{ eV} \) versus cell volume for the case of Ni\textsubscript{2}MnAl. The crosses are calculated values, the curve corresponds to the Murnaghan equation.}
\end{figure}

B. Electronic properties of Ni\textsubscript{50}Mn\textsubscript{x}Al\textsubscript{50-x}

The magnetic moments increase for the FM structures when Al is gradually replaced by Mn. Mn carries the
main magnetic moment of 3.33 $\mu_B$ per atom in the case of FM Ni$_2$MnAl. Ni atoms only contribute 0.36 $\mu_B$, Al -0.03 $\mu_B$. These values correspond to other theoretical results: 3.30 $\mu_B$, 0.38 $\mu_B$, and -0.06 $\mu_B$, respectively (Ref. 22). The calculated total magnetic moment of 4.02 $\mu_B$ fits the experimental observation of 4.19 $\mu_B$.\textsuperscript{14}

The magnetic ground state for Ni$_2$MnAl is ferromagnetic. For higher Mn concentrations, the AFM state is preferred. For lower concentrations, the total magnetic moment of the compound decreases and FM and AFM become degenerated. The total energy is plotted in Fig. 5 versus the fraction of Mn for the FM and the AFM state. The difference in energy multiplied by a factor of 1000 is also given. One can determine from this plot, that the FM state is stable in the range from 14 to 31 at.% Mn. This fact is important for the application of Ni-Mn-Al, because one can only induce a magnetic driven shape change in the FM state. In Heusler alloys (X$_2$MnZ) containing X = Ni the interaction between Mn atoms is mediated by the Ni sublattice as Kübler et al.\textsuperscript{28} have shown. Besides, they found that in the case of Z = Al the FM state is further stabilized. In other Heusler alloys, the interaction is mediated by the Z-atoms, resulting in an AFM ground state. This can explain the change to AFM by replacing Al by Mn atoms.

The magnetic moments also vary with the c/a ratio. Although Mn contributes the main magnetic moment, the curve shape of the total magnetic moment is determined by the Ni contribution (see Fig. 6). This fact underlines the relevance of the Ni atoms for the coupling of magnetic moments. The magnetic moment of FM Ni$_2$MnAl and the Ni contributions have got a minimum at the cubic structure, while the magnetic moments of Mn and Al reach a maximum for c/a = 1. The total magnetic moment rises by a tetragonal distortion, but drops again for c/a > 1.5, just when the E(c/a) curve (see Fig. 4) flattens. One can see a strong relationship between structural stability and its magnetic moment.

In order to obtain a closer insight into the electronic properties and the resulting magnetic and mechanical properties, we examined the density of states exemplified for Ni$_2$MnAl. Figure 7 shows the DOS of FM Ni$_2$MnAl including the individual atomic contributions. Mainly the Ni DOS (dotted line) accounts for the total DOS. But spin-up and down states are approximately balanced, so that only a small magnetic moment results from the Ni atoms. The total magnetic moment is dominated by the Mn atoms, the electrons of which occupy almost solely spin-up states. The two main peaks below the Fermi level (E$_F$) in the Mn DOS coincide with peaks of the Ni DOS, proving the strong coupling between these atoms. The exclusive occupation of spin-up states can be explained by the five single d-electrons of the Mn atoms. Due to hybridization, the magnetic moment is slightly lower compared to an isolated Mn atom. The Al contribution to the total DOS and magnetic moment is negligible.
C. Modulated martensitic structures

The system Ni-Mn-Al is rich in martensitic phases. Below we present the results for the modulations 2M, 10M, and 14M. These phases are found experimentally in alloys near the simulated composition Ni$_2$MnAl.

The 2M phase is a monoclinic distortion of the st cell shown in Fig. 8 (left) with an angle $\theta$ between $a'$ and $c' > 90^\circ$. For Ni$_2$MnAl, the lattice parameters relax to $a' = c' = 0.4288$ nm and $b' = 0.5121$ nm, $\beta_{2M} = 105^\circ$. The angle is a little larger than suggested by Kainuma et al.\textsuperscript{17} from experimental data and also as derived from transmission electron microscopy (TEM) images of a sample with comparable composition (see below). The total energy per formula unit (f.u.) is slightly higher than for the cubic Heusler structure for this composition. But experiments show (see, e.g., Ref. 17) that the 2M phase occurs at lower Al content (approx. 20 at.%) in bulk material. It is assumed that the 2M structure is twinned. Thus, we performed calculations on a structure of two st cells attached to each other in [110] direction with opposed angle $\theta$. In fact, the relaxation yields a smaller total energy per formula unit ($\Delta E = 38$ meV/f.u.). This should hold for the 10M and 14M structures as well. It should be mentioned here that twinning is an essential feature for the shape memory effect.

The 10M structure can be regarded as a structure with the \{110\} planes displaced in the [110] direction along a static wave.\textsuperscript{10} The amplitudes of the Al-Mn and Ni planes relax to 18.3 pm and 20.6 pm, respectively (see Fig. 9). An equivalent way to describe the 10M phase is by a 5-layer structure with stacking order $(32\overline{1})$ (see, e.g., Morito et al.\textsuperscript{16}). The calculated lattice parameters read $a' = 0.4159$ nm, $b' = 0.5643$ nm, $c' = 2.072$ nm resulting in a $c/a$ ratio of 0.961. The cell stays almost orthogonal with an angle $\beta_{10M} = 90.5^\circ$. The 10M phase is metastable with the Heusler cubic structure only 1.2 meV/atom lower in energy. The explanation of the metastability of the 10M phase (with a $c/a$ ratio < 1.0) can be found in the electronic structure. In Fig. 10, the DOS around $E_F$ for the 10M structure compared to the Heusler cubic structure and a tetragonal structure with $c/a = 0.950$ near $c/a(10M)$ is shown. The distortion into 10M moves states just below $E_F$ to lower energies and states just above $E_F$ to higher energies. This suggests additional binding mechanisms in the 10M structure. To analyze this bonding further, we investigated the charge distribution in the Ni planes (see Fig. 11). While the charge density is distributed symmetrically around the Ni atoms in the cubic L2$_1$ structure (Fig. 11 bottom), in the 10M structure there are jagged bands of elevated density between a certain configuration of Ni atoms. This fact suggests additional covalent bonding between these...
FIG. 10: DOS around the Fermi level for the 10M structure of Ni$_2$MnAl (solid line) in comparison with the cubic (dotted line) and a tetragonal structure with $c/a = 0.950$ (dashed line).

FIG. 11: (Color online) Charge distribution in a Ni plane of the 10M structure (top) in comparison with the L2$_1$ structure (bottom) of Ni$_2$MnAl. The charge density is shown in the range from -190 to -410 eV/nm$^3$.

atoms and seems to be responsible for the stabilization of the 10M phase.

In the 14M structure, consecutive $\{110\}$ planes build up the stacking sequence (52), as shown in Fig. 8 (right). The lattice parameters relax to $a' = 0.4076$ nm, $b' = 0.4733$ nm, and $c' = 2.8386$ nm. From this follows $a = 0.575$ nm and $c = 0.4733$ nm resulting in $c/a = 0.82$. The 14M cell is orthorhombic with $\beta_{14M}=95.4^\circ$. The calculated lattice constants are slightly smaller than the experimental ones by Kainuma et al.,$^{11}$ however, they examined off-stoichiometric compositions with Al < 20 at.%. The total energy of the 14M phase suggests that it is only metastable but it is not possible to directly compare with the energies of the calculated structures above as the precision for the simulation of 14M had to be decreased due to computational limitations.

The 2M and 14M phases are indeed found experimentally side by side in a thin film sample produced by molecular beam epitaxy (MBE) with a composition around Ni$_{52}$Mn$_{31}$Al$_{17}$.$^{29}$ Cross-sectional TEM micrographs of the sample show stripes of two different martensitic phases (see Fig. 12). Electron diffraction proves the existence of the 2M phase in the bright stripes and of the 14M phase in the dark stripes. High-resolution images of the dark areas reveal the stacking sequence (52), which complies with 14M (see Fig. 13).

With the calculated lattice parameters X-ray diffractograms can be simulated. For this purpose, we use the powder crystallography software Rietveld.$^{31}$ In Fig. 14, the calculated diffractograms of the 2M and 14M phase of Ni$_2$MnAl are shown in comparison with the experi-
mentally obtained diffractogram of the aforementioned thin film sample. The theoretical results reveal that the experimental diffractogram consists of a mixture of the 2M and 14M phases. A mixture was expected because the X-ray beam averages over a spot size of about 0.5 mm in diameter and hits several stripes of both phases (see Fig. 12). The experimentally observed reflex at $2\theta = 46^\circ$ is very small in the simulated diffractogram. This could be due to comparing highly oriented grains typical for MBE martensitic films with powder simulation and/or due to the chosen atomic form factors. However, the positions of the reflexes reveal correct information. The experimentally observed reflexes are shifted to smaller angles, which can be explained by off-stoichiometry and lower ordering in the lattices. Both factors lead to higher monoclinic angles $\beta$ and larger lattice constants. Thus, spacings of atomic planes increase, which results in smaller angles in the X-ray diffraction. In order to show these effects, the length of the lattice vector $c'$ for the 14M structure was elongated by 1% and the angle $\beta_{2M}$ was reduced to 101°. Accordingly, the positions of the reflexes are shifting to lower angles as indicated by the vertical markers in Fig. 14, matching the experimental diffractogram.

**D. Lattice dynamics**

Phonon-dispersion curves calculated for the [110] direction of the Heusler L2$_1$ structure of ferromagnetic Ni$_2$MnAl are shown in Fig. 15. A complete softening of the transverse-acoustic TA$_2$ phonon mode is found in the range between $\zeta = 0.25$ and $\zeta = 0.4$. This softening characterizes the instability of the cubic structure with respect to a shear displacement of the atoms. The character of the soft mode corresponds to the pattern of atomic displacements of the modulations 2M, 10M and 14M. The wave vector $\zeta = 0.25$ represents a modulation with a period of 8 atomic planes (2M structure), while $\zeta = 0.4$ characterizes the 10M modulation. Finally, the 14M modulation can be characterized by the wave vector $\zeta = 2/7$ which also lies in the range between $\zeta = 0.25$ and $\zeta = 0.4$. In addition, we note that the coupling of the acoustic modes TA$_1$ and LA with low-lying optical modes of Ni is important with respect to the formation of the modulated phases. This was analyzed earlier for the case of Ni$_2$MnGa$^{34}$. The origin of the phonon softening in Fig. 15 can be explained in terms of strong electron-phonon coupling and the Kohn anomaly$^{35}$.

**E. Elastic constants**

The calculated phonon dispersion relations allow to estimate the sound velocities propagating in the crystal.
TABLE IV: Theoretical elastic constants of Ni$_2$MnAl in comparison to those of Ni$_2$MnGa, calculated and measured. The theoretical values have been obtained from the sound velocities listed in Tab. III using relations of the elastic constants taken from Ref. 37.

<table>
<thead>
<tr>
<th>Material</th>
<th>C$_{11}$</th>
<th>C$_{12}$</th>
<th>C$_{44}$</th>
<th>C$_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$MnAl</td>
<td>193</td>
<td>129</td>
<td>102</td>
<td>263</td>
</tr>
<tr>
<td>Ni$_2$MnGa$^a$</td>
<td>139.4</td>
<td>122.6</td>
<td>91</td>
<td>222</td>
</tr>
<tr>
<td>Ni$_2$MnGa$^b$</td>
<td>152</td>
<td>143</td>
<td>103</td>
<td>250</td>
</tr>
</tbody>
</table>

$^a$theor., Zayak et al., Ref. 34  
$^b$exp., Worgul et al., Ref. 37

The two transverse and the longitudinal sound velocities of Ni$_2$MnAl have been obtained from the initial slopes ($\zeta \rightarrow 0$) of the acoustic modes TA$_1$, TA$_2$, and LA, respectively. These values are listed in Table III in comparison with the corresponding sound velocities of Ni$_2$MnGa. To our knowledge, there are no data in the literature about phonon and elasticity measurements for Ni$_2$MnAl. Our phonon calculation gives accurate results for the sound velocities obtained from the TA$_1$ and LA phonon modes. While in the case of the soft mode TA$_2$ we found it difficult to define the initial slope of the curve. One can expect a variation of the value due to the uncertainty of the slope in the range of $\pm 20\%$. The difference in sound velocities of Ni$_2$MnAl and Ni$_2$MnGa can be explained by the lower atomic mass of the aluminum atoms in comparison to gallium, leading to higher lattice frequencies and faster sound velocities.

Table IV gives a list of the elastic constants of Ni$_2$MnAl associated with the sound velocities by:

$$v_L = \sqrt{C_L/\rho} = \sqrt{(C_{11} + C_{12} + 2C_{44})/2\rho},$$  
$$v_{TA_1} = \sqrt{(C_{11} - C_{12})/2\rho},$$  
$$v_{TA_2} = \sqrt{(C_{44})/\rho}.$$  

The density is derived from the calculated lattice constants to $\rho = 6.722$ g/cm$^3$. The values are given in comparison with those of Ni$_2$MnGa. Again one can expect some deviation from the values for the constants C$_{11}$ and C$_{12}$ which are defined by the soft phonon mode TA$_2$, while the C$_L$ and C$_{44}$ might be as accurate as the calculated phonon spectra.

IV. SUMMARY

In this paper, we present results of ab initio calculations of the magnetic shape-memory alloy Ni$_{50}$Mn$_x$Al$_{50-x}$ in the range $0 \leq x \leq 50$ for FM and AFM structures. We found that the cell volume does not change much by varying the Mn content, the c/a ratio stays close to 1. Only for AFM structures with high Mn concentrations a c/a ratio > 1.2 is more stable than the cubic structure.

We estimated compression moduli for the alloys by calculating the energies for different fixed cell volumes and fitting the energy-volume pairs to the Murnaghan equation. The values are close to former theoretical moduli, where available.

The magnetic ground state for Ni$_2$MnAl is FM, consistent with other theoretical and experimental results. The FM structure remains the ground state in the range from 14 to 31 at.% Mn. For higher Mn concentrations, the AFM structure is preferred. For lower Mn concentration, the state of AFM and FM is almost degenerated. This result is important for the application of Ni-Mn-Al because only the FM structure can be used as a magnetic driven shape-memory device.

The magnetic moment is located mostly at the Mn atom sites with $\mu > 3\mu_B$. Ni has only a small magnetic moment, Al is almost negligible. But Ni atoms are responsible for the FM coupling of the Mn moments in the ordered Heusler structure. The magnetic moments can be explained by the DOS of Ni$_2$MnAl: While Ni states are almost equally distributed in spin-up and down components, the bonding Mn (3d) states are almost all located in the spin-up part.

The modulated martensitic structures 2M, 10M, and 14M are simulated for Ni$_2$MnAl. All these phases are metastable at this composition and have c/a ratios < 1. As shown for the 10M structure, the stabilization of these phases can be explained by additional (covalent) bonding between certain Ni-atoms, as expressed by the DOS and the charge distribution in the Ni planes.

Simulated X-ray diffractograms of the martensitic structures are compared with experimental ones and give additional evidence of the co-existence of the 2M and the 14M phase in thin films with a composition of Ni$_{52}$Mn$_{31}$Al$_{17}$, deposited by MBE. Cross-sectional TEM investigations provide further proof for this fact.

The calculated phonon dispersion relations for the [110] direction show that the cubic L$_2_1$ structure is unstable with respect to atomic displacements leading to the modulations 2M, 10M, and 14M. We conclude that the modulations simulated in this work have their origin in two physical phenomena: The Kohn anomaly, which makes the cubic structure unstable, and the stabilization of these modulations due to charge transfer related to the covalent bonding in the sublattice of Ni mediated by the p electrons of Al.

Elastic constants are calculated from the initial slopes of the acoustic modes. The values are in good agreement with theoretical and experimental data of Ni$_2$MnGa. Experimentally derived elastic constants for Ni$_2$MnAl deserve further investigation.

Our results show that the ab initio theoretical approach is a valuable tool to identify and characterize unknown and complex crystallographic structures in experimental samples.
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Figure 2
Figure 3
Figure 4

\[ \Delta E_0 \text{ (meV/atom)} \]

\( \frac{c}{a} \)
Figure 5
Figure 6
Figure 7
Figure 10
Figure 12
Figure 14
Figure 15