Local atomic configuration approach to the nonmonotonic concentration dependence of magnetic properties of Ni(2)Mn(1+x)Z(1-x) (Z = In, Sn, Sb) Heusler alloys

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Local Atomic Configuration Approach to the Nonmonotonic Concentration Dependence of Magnetic Properties of
Ni$_2$Mn$_{1+x}$Z$_{1-x}$ (Z=In,Sn,Sb) Heusler Alloys

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Abstract
The Ni$_2$Mn$_{1+x}$Z$_{1-x}$ Heusler alloys, where Z=In,Sn,Sb are attractive candidates for shape memory applications. The effect is directly related to their magnetic properties. We have studied these systems by ab-initio calculations and experiments, focusing on magnetic moments and exchange-bias fields. The calculations indicate that the composition dependence of the total magnetic moment is due to competing ferromagnetic and anti-ferromagnetic alignment between Mn atoms on different sublattices and with different local environments. This phenomenon can also explain the composition dependence of the exchange-bias effect.

Keywords: Heusler phases; ferromagnetic shape memory alloy; magnetic thin films; magnetic structure; ab initio calculation

Heusler alloys constitute a family of materials with numerous interesting properties [1], such as half-metallicity, magnetocaloric and magnetic shape memory effects, which are related to their magnetic properties. Some of the most spectacular effects, like the giant exchange-bias (EB) [2] and inverse magnetocaloric effects [3], low Gilbert damping [4],

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or shell-ferromagnetism [5], are observed in off-stoichiometric Heusler alloys. In such
cases, the coexistence of domains with different local environments of the atoms, and the
interaction between them, play a major role.

In this work, we study magnetic properties in the Heusler alloys Ni$_2$Mn$_{1+x}$Z$_{1-x}$
(Z=In,Sn,Sb). These alloys are interesting candidates for shape memory applications
[1]. Application of a magnetic field induces a structural transformation from an antiferro-
magnetic (AFM) martensite phase to a ferromagnetic (FM) cubic austenite phase [1].
This effect depends strongly on the difference in the magnetization of the phases, which
is higher in the cubic austenite phase [6, 7].

The magnetization of these alloys have been studied experimentally by Ito et al. as a
function of the alloy composition. The crystal structure of the austenite phase, shown in
Fig. 1, can be viewed as four interpenetrating fcc (face centered cubic) sublattices, where
X€(\(\frac{1}{4}, \frac{1}{4}, \frac{1}{4}\)), Y€(0,0,0) and Z€(\(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\)). These sublattices are occupied
as X=Ni, Y=Mn and Z=In/Sn/Sb. By substituting a fraction of the Z-atoms with Mn
atoms, a qualitative difference in total magnetic moment (\(M_{\text{tot}}\)) vs composition (\(x\)) was
observed in the Ni$_2$Mn$_{1+x}$Z$_{1-x}$ systems [8, 9], as shown in Fig. 1. Increasing the Mn
content in the Z=In system leads to a monotonic increase of \(M_{\text{tot}}\). However, the trend
is opposite for the Z=Sb system, with a monotonous decrease of \(M_{\text{tot}}\). An interesting
intermediate situation is found for Z=Sn, where the concentration dependence has a
nonmonotonic character, with a minimum at about \(x = 0.2\).

The role of magnetic interactions between Mn atoms occupying two different sublat-
tices in cubic Ni-Mn-based Heusler alloys has been studied in previous works. Sokolovskiy
et al. investigated by \textit{ab-initio} calculations the influence of chemical disorder on magnetic
properties of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ alloys [10], but they could not confirm the non-monotonic
behavior of \(M_{\text{tot}}(x)\). In the theoretical work of Entel et al., the interactions between
the spins on the original Y-sublattice (Mn$^+_Y$) and on the Z-sublattice (Mn$^+_Z$) or on the
X-sublattice (Mn$^+_X$) in Ni-Mn-Z alloys where shown to have exclusively antiferromagnetic
character [11]. This can not explain non-monotonic behavior of the \(M_{\text{tot}}(x)\). Recently,
Cavazzini et al. reported on the influence of Sn composition on the magnetic properties
of cubic austenite Ni$_{1.92}$Mn$_{1.44}$In$_{0.64}$Sn$_x$ alloys [12]. They examined two magnetic
states, where the alignment of Mn moments on the Y and Z sublattices were either com-
pletely ferromagnetic or antiferromagnetic. In the In-rich case, the calculations fit the
experimental values, where the Mn$_2$ atoms were ferromagnetic. However, in the case of
the Sn-rich alloys, neither completely ferromagnetic nor antiferromagnetic configurations
did fit the experiment, suggesting the need of a third approach.

In this work we present results from \textit{ab-initio} calculations and experiments to in-
vestigate the origins of these different behaviors in the cubic austenite phase. We also
present measurements of the exchange-bias effect for the Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ alloy at several
compositions of the cubic phase. We show that the presence of competing FM and AFM
can explain the concentration dependence of the magnetization for Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ al-
loys. Simultaneously, our model correctly describes Ni$_2$Mn$_{1+x}$In$_{1-x}$ and Ni$_2$Mn$_{1+y}$Sn$_{1-x}$
alloys.

We have performed \textit{ab-initio} calculations for Ni$_2$Mn$_{1+x}$Z$_{1-x}$ (Z=In,Sn,Sb) using
the exact muffin-tin orbitals (EMTTO) method [13, 14, 15] with the Perdew-Burke-Emzerhof
exchange-correlation functional [16]. In order to model the alloy system, one may use
large supercells [17, 18, 19] to create a unique local environment for each atom. However,
this approach may turn out very time consuming, and we have employed an alternative
Figure 1: Magnetic moment (in Bohr magneton per formula unit) obtained by CPA calculations compared with experiment (Ref. [9]). Inset - L2₁ crystal structure of Ni₂MnZ Heusler alloys.

Figure 2: Total energy calculated for Ni₂Mn₁₋ₓZ₁₋ₓ alloys (Z=In,Sn,Sb) as a function of composition, x, and magnetic state, ξ. The energy scale is relative to the FM state (ξ = 1). The lowest energy is represented by “o” symbols.
route, the Coherent Potential Approximation (CPA) [20]. In the framework of the CPA one replaces each atom in the alloy by an effective atoms with scattering properties determined self-consistently. This allows the size of the simulated system to be reduced to a single unit cell, although all local fluctuations of the composition and spin orientation are averaged out [21]. We used a basis of $s$, $p$, $d$, $f$ muffin-tin orbitals to expand the Kohn-Sham orbitals. To sample the Brillouin zone, we used a $21 \times 21 \times 21$ $k$-point mesh from which 946 points were chosen by a Monkhorst-Pack routine for the irreducible part of the Brillouin zone. Total energy was converged within 0.1 $\mu$Ry during the self-consistency cycles. We used a semi-elliptical contour in the complex energy plane with 32 energy points spanning 2.5 Ry below the Fermi level, which included the $4d$ states of the Z atom.

Epitaxial thin films with $x = 0$, $0.2$, $0.36$ were sputter deposited on MgO(001) substrates. Details on the preparation, structural and magnetic properties of thin films can be found in Supplementary Materials.

In Fig. 1 we show the magnetic moment of the cubic $L2_1$-$Ni_2Mn_{1+\delta}Z_{1-\delta}$ alloys as obtained with the CPA applied to the Z-sublattice, compared with the experimental data in Ref. [9]. For all systems, the magnetic moments of the Mn atoms at the Y-sublattice are coupled ferromagnetically to each other. In the $Ni_2Mn_{1+\delta}In_{1-\delta}$ alloys, we find the Mn$_Z$ atom to align its magnetic moment in parallel to the total magnetic moment (FM coupling) at all compositions. Increase of concentration then translates to an increase of the total magnetic moment, which reproduces the available experimental data well. For the case $Z=Sb$, the decrease of the magnetic moment is captured as well. However, the nonmonotonic behavior for $Z=Sn$ is not reproduced. Nevertheless, we do observe how the magnetization of the Mn$_Z$ atoms are reversed at high concentrations. This indicates the presence of competing FM and AFM interactions in the alloys, which are not properly accounted for by the single-site CPA. We therefore extend our model to include disorder of the local Mn$_Z$ moments.

In order to allow for magnetic disorder, we turn to the partially disordered local moment (PDLM) approximation [22] to model a random mixture of Mn$_Z^\uparrow$ and Mn$_Z^\downarrow$ atoms on the Z-sublattice. The chemical formula of the sublattice is then expanded to read $Z_{1-\delta}(Mn_{1+\delta}\text{Mn}_Z^{\uparrow}-\xi)_x$, where $0 \leq \xi \leq 1$ is the concentration of Mn$_Z^\uparrow$ atoms. An FM configuration corresponds to $\xi = 1$, while $\xi = 0.5$ corresponds to an equal mixture of Mn$_Z^\uparrow$ and Mn$_Z^\downarrow$, which represents a completely disordered magnetic state. At $\xi = 0$, all Mn$_Z$ are antiferromagnetically aligned to the Mn atoms on the Y-sublattice.

We then need to determine the appropriate value of $\xi$ for each composition, $x$. Total energy calculations for different values of $\xi$ and $x$ yield a minimum for Mn$_Z$ in either FM ($\xi = 1$) or AFM ($\xi = 0$) configuration, as shown in Figure 2, since they correspond to the magnetically ordered model. In order to take the disorder into account we therefore represent the nearest neighbor shell of the Mn$_Z$ atoms as a statistical distribution of cuboctahedrons, populated by $0 \leq n \leq 12$ Mn$_Z$ atoms, illustrated Fig. 3(a). The magnetic configuration of the Mn$_Z$ atoms in the nearest neighbor shell is then allowed to vary as a function of $n$. The statistical weight of each cuboctahedron in the model is given by the probability, $P$, of finding a cuboctahedron containing $n$ Mn$_Z$ atoms, and can be written as: [23]

$$P(n,x) = \frac{N!}{(N-n)!n!}(1-x)^{N-n}x^n,$$

where $N = 12$ is the number of sites in a cuboctahedron. This probability function is
Figure 3: (a) Atomic configurations used to represent the Ni$_2$Mn$_{1+x}$Z$_{1-x}$ alloys in the probability distribution $P(n, x)$. The number $n$ of Mn$_Z$ atoms (orange) on the Z-sublattice is related to the alloy composition as $x = n/12$. (b) $P(n, x)$ calculated from Eq. (1), corresponding to cuboctahedrons populated by $n$ Mn$_Z$ atoms. The star symbols denote the total probability, $S^Z(x)$, of cuboctahedrons with FM-aligned Mn$_Z$ atoms.
plotted as a function of composition in Fig. 3(b), for various values of \( n \). Eq. (1) and its modifications are commonly used to calculate the distribution of the local atomic configurations determined by the nuclear magnetic resonance spin-echo measurements [24, 25].

We calculate the magnetic configuration of the Mn\( _Z \) atoms by CPA, treating the Z sublattice as a homogenous mixture of Mn\( _Z \) and Z atoms, with the concentration \( x = n/12 \). For Z=In we find FM alignment for all values of \( n \). In the case of Z=Sn the orientation is FM for \( n \geq 6 \), and for Z=Sb when \( n \geq 9 \). We may now sum up the probability, \( S \), of finding a cuboctahedron with FM-aligned Mn\( _Z \) atoms, as follows:

\[
S_{\text{In}}(x) = \sum_{n=0}^{12} P(n, x), \quad S_{\text{Sn}}(x) = \sum_{n=6}^{12} P(n, x), \quad S_{\text{Sb}}(x) = \sum_{n=9}^{12} P(n, x).
\]

The total probability, \( S \), is used as the PDLM order parameter by setting \( S = \xi \) so that the Z sublattice is modelled as:

\[
Z_{1-x}(\text{Mn}^+_Z\text{Mn}^-_{1-S})_x.
\]

The values of \( S_Z \) are plotted as a function of the concentration \( x \) in Fig. 3(b).

Figure 4(a) presents the concentration dependence of the experimental [9] (full symbols) and calculated (half-open symbols) total magnetic moments of the cubic Ni\(_2\)Mn\(_{1+x}\)Z\(_{1-x}\) (Z=In,Sn,Sb) alloys, where the Z sublattice is modelled based on Eq. (2). For Z=In, \( \xi = 1 \) at all compositions, meaning that we correctly recover the linear concentration dependence.

In contrast, for Z=Sn we reproduce a nonlinear concentration dependence of the magnetization. For low \( x \) the \( M_{\text{tot}} \) decreases, reaching a minimum, followed by an increase up to the maximum value, which is reached for the Ni-Mn compound. The minimum of the calculated curve is found at higher values of \( x \) than in the experimental data. The quantitative disagreement is likely because of a higher concentration of Mn atoms on the Z sublattice in the real alloys. This is due to metastability and tendency to phase decomposition of Z=Sn alloys [26], which could be more likely with increasing Mn composition [27]. Therefore, one can expect a slightly higher concentration of FM-aligned Mn\( _Z \) atoms in the real alloys. In fact, the phase separation and the existence of FM and AFM clusters in Ni-Mn-Sn alloys were comprehensively studied in Refs. [28], where the authors concluded that the upturn in the total magnetization is determined by the presence of nanoscale magnetic phase separation into FM and AFM regions. Our results demonstrate that the effect is intrinsic for the considered alloys, and it should be seen in Ni\(_2\)Mn\(_{1+x}\)Sn\(_{1-x}\) samples without any additional thermal treatment aimed at phase decomposition.

For the case of Z=Sb, we reproduce the linear decrease of \( M_{\text{tot}}(x) \) with concentration, in line with the available experimental data. We also observe a nonmonotonic concentration dependence at higher values of \( x \). It is associated with a more stable AFM coupling between Mn and Mn\( _Z \) atoms in the Z=Sb alloy. A similar effect is observed in the austenite phase of Ni-Mn-Ga magnetic shape memory alloys [29, 30].

A suggestion for the reason behind this effect is the change in the electronic density of state (DOS) as the concentration of Mn\( _Z \) atoms changes in the studied alloys (Figs. S17-S19 in Supplementary Materials). In the FM state, as the concentration of Mn\( _Z \) increases, there is a transfer of the spectral weight of the spin up peak located between \( -0.1 \) and \( -0.05 \) Ry below the Fermi energy from higher to lower energy. In the antiferromagnetic configuration, the DOS is virtually unaffected. Thus, increasing concentration of Mn\( _Z \) should shift the energy balance in favor of the FM state.
Figure 4: (a) Total magnetic moment $M_{\text{tot}}$ of Ni$_2$Mn$_{1+x}$Z$_{1-x}$ alloys (Z=In,Sn,Sb). The experimental [9] and calculated data are shown by solid and half-open symbols, respectively. The non-shaded part of the plot corresponds to the L2$_1$ phase stability composition range. (b) The occupation level of Z(Sn)-sublattice by Mn atoms with FM (closed symbols) and AFM (open symbols) spin orientation in Ni$_2$Mn$_{1+x}$Sn$_{1-x}$. The star symbols represent the $H_{EB}$ measured at 5 K for Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0, 0.2, 0.36$) thin films.
The coexistence of interacting FM and AFM domains leads to the exchange-bias (EB) effect [31, 2, 32]. The magnitude of EB can be determined by a shift of the hysteresis loop \( (H_{EB}) \) (Figs. S3-S4 in Supplementary Materials). We have therefore measured \( H_{EB} \) in Ni\(_2\)Mn\(_{1+x}\)Sn\(_{1-x}\) thin films at low temperature (5 K).

The results are shown in Fig. 4b. In the stoichiometric case, \( x = 0 \), \( H_{EB} \) is almost zero. \( H_{EB} \) then increases significantly at higher concentrations to the level of 5 Oe. In the light of our theoretical calculations, we may explain these experimental results as follows (see Figs. S5-S8 in Supplementary Materials). Since the Y-sublattice is fully occupied by the FM oriented Mn atoms, while the Z-sublattice is only partially occupied by the AFM oriented Mn atoms, the FM phase can be considered as a matrix. Therefore, the EB effect, and hence, the magnitude of \( H_{EB} \), should depend on the number of AFM domains. The measurements may be compared to the calculated occupation level of the Z-sublattice by Mn up/down atoms. As the occupancy of Mn on the Z-sublattice increases, the fraction of FM coupled Mn\(_Z\) atoms increases monotonically, while the fraction of AFM coupled Mn\(_Z\) atoms has a non-monotonic behaviour. The maximum fraction of AFM-Mn\(_Z\) atoms is reached at the composition \( x = 0.36 \). At increasing Mn content, the fraction of AFM coupled Mn atoms on the Sn-sublattice decreases. The calculated composition of Mn\(_{36}\) matches the measured \( H_{EB} \) relatively well.

In summary, we have carried out experiments and ab-initio calculations for Ni\(_2\)Mn\(_{1+x}\)Z\(_{1-x}\) (Z=In,Sn,Sb) alloys. We find that the composition dependence of the total magnetization can be qualitatively explained with a simple statistical model which includes Mn atoms with both FM and AFM orientations. Our model correctly reproduces the experimentally reported trends of increasing magnetization for Ni\(_2\)Mn\(_{1+x}\)In\(_{1-x}\) and decreasing magnetization for Ni\(_2\)Mn\(_{1+x}\)Sb\(_{1-x}\), with increasing Mn content.

For Ni\(_2\)Mn\(_{1+x}\)Sn\(_{1-x}\) we also reproduce the nonmonotonic composition dependence, which indicates that competing FM and AFM Mn atoms are responsible. This is also supported by measurements of the exchange-bias field in thin films of Ni\(_2\)Mn\(_{1+x}\)Sn\(_{1-x}\), which also seem to support the notion of competing FM and AFM interactions.

It should be noted that our computational model only takes into account the mixture of FM and AFM Mn atoms in a mean-field sense. It does not explicitly include local environment effects, such as magnetic and structural short-range order or lattice relaxations. A continuation of our work would be supercell calculations to include such effects, in order to improve the quantitative agreement. Nevertheless, the qualitative success of our simple model indicates that it captures the most important physical effect in these alloys: that of competing FM and AFM interactions.

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Supplemental Material: Local Atomic Configuration Approach to the Nonmonotonic Concentration Dependence of Magnetic Properties of Ni$_2$Mn$_{1+x}$Z$_{1-x}$ ($Z = \text{In, Sn, Sb}$) Heusler Alloys

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I. EXPERIMENTAL DETAILS

Thin film growth has been performed in a magnetron sputtering system at 400 °C in a $2 \times 10^{-4}$ mbar Ar pressure. The films were deposited on single crystalline MgO(001) substrates by means of co-sputtering from Ni, Mn, and MnSn targets. The composition of the films was controlled by the choice of deposition rates from the targets. To analyse the composition and thickness of the films the x-ray fluorescence (XRF) method was used - the results are presented in Tab. I.

TABLE I: Effective composition and thickness of Ni$_{2}$Mn$_{1+x}$Sn$_{1-x}$ thin films.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Ni</th>
<th>Mn</th>
<th>Sn</th>
<th>thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.08</td>
<td>0.97</td>
<td>0.95</td>
<td>170</td>
</tr>
<tr>
<td>0.20</td>
<td>2.02</td>
<td>1.17</td>
<td>0.81</td>
<td>290</td>
</tr>
<tr>
<td>0.36</td>
<td>1.98</td>
<td>1.37</td>
<td>0.65</td>
<td>470</td>
</tr>
</tbody>
</table>

X-ray diffractometry (XRD, Cu-K$\alpha$) was conducted for determining the crystal structure of the films. The XRD patterns for Ni$_{2}$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.0, 0.2, 0.36$) thin films (Fig. S1) reveals Ni-Mn-Sn(001) orientation on MgO(001). The full width at half maximum of Ni-Mn-Sn peaks are about 0.3° for (200) and (400) reflections what confirms that the chemically ordered structure has been achieved.

FIG. S1: X-ray diffraction patterns of Ni$_{2}$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.0, 0.2, 0.36$) thin films measured in conventional $\theta - 2\theta$ geometry.
Zero field cooling (ZFC) and field cooling (FC) thermomagnetization curves of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.0, 0.2, 0.36$) thin films, shown in Fig. S2, were measured in magnetic field of 100 Oe on the MPMS-XL magnetometer. For all the concentrations the Curie temperature is below 350 K and the splitting between ZFC and FC curves is presented. The splitting between ZFC and FC curves is a signature of coexistence of the ferro- and antiferromagnetic interactions.

![Graphs](image)

**FIG. S2**: Temperature dependence of magnetization (ZFC, FC) of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.0, 0.2, 0.36$) thin films measured at 100 Oe.

### II. RESULTS OF MAGNETIC MEASUREMENTS - EXCHANGE BIAS EFFECT

Figure S3 compares magnetic hysteresis loops of thin films of Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.0, 0.2, 0.36$) Heusler alloys. The magnetic field was applied in the plane of the films. The shift of the hysteresis loops refers to the exchange bias effect (EB).

Since the EB effect is small we have to ensure there are no artefacts from trapped flux in the superconducting coil. For this purpose, we applied a measuring sequence with the magnet reset option after field cooling the samples. During the magnet reset the superconducting coil is warmed above the critical temperature and the trapped fields in the magnet are eliminated. Additionally, to ensure the observed EB effect originates from the samples we performed three sets of magnetic measurements: field cooling in positive field (FC 5 kOe), field cooling in negative field (FC -5 kOe) and zero field cooling (ZFC).

Temperature dependence of coercivity $H_C$ and exchange bias field $H_{EB}$ for $x = 0.0, 0.2, 0.36$ are shown on Fig. S4 upper and lower panel, respectively. The coercivity $H_C$ of stoichiometric sample ($x = 0.0$) is almost independent of its history. In all three modes: FC 5 kOe, FC
FIG. S3: Hysteresis loops at 5-35 K after the samples were cooled in 5 kOe, -5 kOe and zero field from 375 K: (a) Ni$_2$MnSn, (b) Ni$_2$Mn$_{1.2}$Sn$_{0.8}$ and (c) Ni$_2$Mn$_{1.36}$Sn$_{0.64}$.

-5 kOe and ZFC, the curves follow the same points and only for the lowest temperature there is a minor difference between them. This difference is related to the very weak exchange bias effect observed only at 5 K for the stoichiometric sample. The sign of the $H_{EB}$ at 5 K corresponds to the cooling field and the magnitude of the exchange bias is slightly smaller after ZFC than FC. For all three modes the $H_{EB}$ decreases to zero as the temperature increases over 5 K.

In the off-stoichiometric ($x = 0.2, 0.36$) case the $H_C(T)$ exhibit monotonic decrease upon increasing temperature and is following the same points for both FC modes. The difference between ZFC and FC temperature dependence of $H_C$ arise from the exchange bias effect.
FIG. S4: Temperature dependence of coercivity $H_C$ and exchange bias field $H_{EB}$ for:

(a) $\text{Ni}_2\text{MnSn}$, (b) $\text{Ni}_2\text{Mn}_{1.2}\text{Sn}_{0.8}$ and (c) $\text{Ni}_2\text{Mn}_{1.36}\text{Sn}_{0.64}$.

The EB effect after ZFC is insignificant, while the temperature dependence of $H_{EB}$ after FC shows decreasing in magnitude as temperature increases, what is connected with reducing coupling at ferromagnetic/antiferromagnetic interfaces with increasing temperature. The sing of the $H_{EB}$ corresponds to the cooling field and is a clear evidence and confirmation of the exchange bias effect.

III. THEORETICAL MODEL OF THE EXCHANGE-BIAS EFFECT IN Ni-Mn-Z

The calculated occupation level of the Z-sublattice by Mn$^\uparrow$ and Mn$^\downarrow$ atoms is shown on Fig. S5.

For Z=In:

- the number of Mn$^\uparrow$ atoms on the Z-sublattice increases linearly with the filling of it,
- there is no Mn$^\downarrow$ atoms in the full range of the composition.

For Z=Sn:

- the number of Mn$^\uparrow$ atoms increases monotonically with the filling of Z-sublattice by Mn atoms,
FIG. S5: The occupation level of Z-sublattice by Mn atoms with FM and AFM spin orientation in Ni$_2$Mn$_{1+x}$Z$_{1-x}$.

- the concentration dependence of the number of Mn$^{\uparrow}$ atoms has a nonmonotonic character with a maximum at $x=0.36$.

For Z=Sb:

- the number of Mn$^{\uparrow}$ atoms increases monotonically with the filling of Z-sublattice by Mn atoms,

- the concentration dependence of the number of Mn$^{\downarrow}$ atoms has a nonmonotonic character with a maximum at $x=0.56$.

Based on the calculated occupation levels of the Z-sublattice by Mn$^{\uparrow}$ and Mn$^{\downarrow}$ atoms (shown on Fig. S5) we propose the model structure of magnetic moments in Ni$_2$Mn$_{1+x}$Z$_{1-x}$ alloys. Magnetic moments of Mn on two sublattices: Y and Z for Ni$_2$Mn$_{1+x}$Z$_{1-x}$, where Z = In, Sn and Sb, are shown on Fig. S6, S7 and S8, respectively. As one can see, for Z=In all the Mn atoms on both sublattices are FM coupled and the fraction of Mn$^{\uparrow}$ increases as the occupancy of the Z-sublattice increases. In the case of Z=Sn, at low concentration almost only Mn$^{\downarrow}$ occupy the Z-sublattice and antiferromagnetic (AFM) domains are present in the ferromagnetic matrix. The coexistence of AFM domains in FM matrix can lead to the exchange-bias effect. With the increase in concentration, the fraction of Mn$^{\uparrow}$ on the Z-sublattice starts to prevail and the number of AFM domains decrease. For Z=Sb the
fraction of AFM domains is higher than for Z=Sn and we assume that the exchange-bias effect in Ni$_2$Mn$_{1+x}$Sb$_{1-x}$ alloys can be stronger.

![Figure S6](image1)

**FIG. S6:** Magnetic moments of Mn atoms on Y- and Z(In)-sublattices for Ni$_2$Mn$_{1+x}$In$_{1-x}$ for $x = 0.0, 0.2, 0.4, 0.6$ and $1.0$.

![Figure S7](image2)

**FIG. S7:** Magnetic moments of Mn atoms on Y- and Z(Sn)-sublattices for Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ for $x = 0.0, 0.2, 0.4, 0.6$ and $1.0$. 
FIG. S8: Magnetic moments of Mn atoms on Y- and Z(Sb)-sublattices for Ni$_2$Mn$_{1+x}$Sb$_{1-x}$ for $x = 0.0, 0.2, 0.4, 0.6$ and $1.0$. 
IV. ADDITIONAL RESULTS OF THE CALCULATIONS

In the Fig. S9 we present total magnetic moment and the magnetic contribution of specific sublattices for Ni$_2$Mn$_{1+x}$Z$_{1-x}$ ($Z =$ In, Sn, Sb) alloys as a function of the composition $x$. A change in the composition almost do not alter the site-specific moment of Mn$_Y$ sublattice, which only slightly decreases with $x$. An increase in the composition has also just a little effect on Z- and Ni-sublattice magnetic moment, where it’s very close to zero or increases slightly, respectively. The main contribution to the changes in the total magnetic moment comes from the moment of Mn at Z-sublattice.

FIG. S9: Theoretical total magnetic moment and the magnetic contribution of sublattices of Ni$_2$Mn$_{1+x}$Z$_{1-x}$ ($Z =$ In, Sn, Sb) Heusler alloys.
FIG. S10: Lattice parameter in the entire composition range for $\text{Ni}_2\text{Mn}_{1+x}\text{Z}_{1-x}$ ($\text{Z} = \text{In, Sn, Sb}$) Heusler alloys with FM and AFM coupling between Mn and Mn$_2$ atoms. The inset shows structure optimization for FM and AFM configuration of $\text{Ni}_2\text{Mn}_{1.2}\text{Sn}_{0.8}$ (energies have been normalized with the respect to the energy minimum of AFM state).

FIG. S11: Density of states for $\text{Ni}_2\text{Mn}_{1+x}\text{In}_{1-x}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) - AFM coupling.
FIG. S12: Density of states for Ni$_2$Mn$_{1+x}$In$_{1-x}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) - FM coupling.
FIG. S13: Density of states for $\text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) - AFM coupling.
FIG. S14: Density of states for \( \text{Ni}_2\text{Mn}_{1+x}\text{Sn}_{1-x} \) \((x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0)\) - FM coupling.
FIG. S15: Density of states for Ni$_{2}$Mn$_{1+x}$Sb$_{1-x}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) - AFM coupling.
FIG. S16: Density of states for Ni$_2$Mn$_{1+x}$Sb$_{1-x}$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$)
- FM coupling.
FIG. S17: The calculated partial density of states Mn_{1n} in FM and AFM configuration for Ni_2Mn_{1+x}In_{1-x} (x = 0.2, 0.4, 0.6, 0.8, 1.0). The lower panel presents difference of energy between AFM and FM configurations.
FIG. S18: The calculated partial density of states Mn$_{Sn}$ in FM and AFM configuration for Ni$_2$Mn$_{1+x}$Sn$_{1-x}$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0$). The lower panel presents difference of energy between AFM and FM configurations.
FIG. S19: The calculated partial density of states Mn$_{Sb}$ in FM and AFM configuration for Ni$_2$Mn$_{1+x}$Sb$_{1-x}$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0$). The lower panel presents difference of energy between AFM and FM configurations.
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