Charge carrier concentration and structural transition temperatures in Heusler alloys Ni$_{50}$Mn$_{36}$Sb$_{14}$-$x$Z$_x$ ($Z$ = Al, Ge; $x$ = 0; 1; 2; 3; 4)

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Abstract. The temperature dependences of magnetization and electrical resistance of the Ni$_{50}$Mn$_{36}$Sb$_{14}$-$x$Z$_x$ ($Z$ = Al, Ge; $x$ = 0; 1; 2; 3; 4) alloys have been used to determine the structural transition temperatures (STT) such as: $M_s$, $M_f$, $A_s$ and $A_f$ (temperatures of the start and finish of martensitic and austenitic transformations, respectively). Effect of various parameters ($e/a$, $V_{cell}$, $n$) on the STT was studied. Using Hall Effect the concentration of charge carriers $n^*$ was obtained and it was found that $n^*$ is not strongly correlated with a behaviour of STT, there is only a general trend with exceptions.

1. Introduction

Traditionally, gadolinium used as a material for the working body in solid-state magnetic refrigerators. However recently so-called shape-memory ferromagnets have become increasingly an alternative, since these alloys can exceed compounds with gadolinium in the value of MCE (magnetocaloric effect) for magnetic field of the same magnitude [1]. Giant values of the MCE are achieved in them due to the structural transformation accompanying the magnetic transition.

There are two main parameters affecting the STT: the ratio $e/a$ (the number of valence electrons per atom) and the volume of the unit cell ($V_{cell}$). In the first case, a direct relationship is observed: the STT increase as $e/a$ increases, and in the second case, the relationship is inverse: as the $V_{cell}$ decreases, the temperatures increase (for example, the relationship between STT and $V_{cell}$ is true for the Ge-doped alloys Ni-Mn-Sn [2], H-doped alloys Ni-Mn-In [3]). However, these trends are not always traced. It was reported about non-monotonic dependence of $M_s$ on $e/a$ in Ni$_{50}$Mn$_{35}$Cu$_{5}$Sn [4] and Ni$_{23}$Cu$_{8}$MnGa [5]. In particular, in [6] it is indicated that the ratio $e/a$ in Ni$_{48}$Mn$_{30}$Sn$_{13}$Si$_{x}$ system alloys ($1 \leq x \leq 4$) does not change with an increase in the Si content and is constantly equal to 8.05; however, the $M_s$ temperatures decrease. In addition, for the Ni-Mn-Ga [7] and Ni-Mn-In-Sb systems [8], it was found that the STT decrease even if the substitution leads to an increase in the $e/a$ ratio and a decrease in the $V_{cell}$. 

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The purpose of this work is to study the Hall Effect, obtaining the concentration of current carriers \( n^* \), and looking for the correlation between \( n^* \) and the STT in Heusler-like alloys \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{14-x}Z_x \) \((Z = \text{Al, Ge}; x = 0; 1; 2; 3)\).

2. Experimental

Ingots were prepared by arc melting in an inert atmosphere and subsequently subjected to annealing at 1100 K for 24 h followed by furnace cooling. Samples for magnetization measurements were cut from preparing ingots by spark cutting. The elemental analysis was performed using an Inspect F scanning electron microscope (FEI Company, USA) equipped with a field-emission cathode and an EDAX spectrometer. The accuracy of elemental analysis is ±2 rel. %. The structural analysis was performed at the Collaborative Access Center, M.N. Mikheev Institute of Metal Physics, UB RAS. X-ray diffraction studies were performed in the Laboratory of Structural Phase Analysis at the Institute of Solid State Chemistry, UB RAS. A STADI-P (STOE, Germany) powder auto diffractometer and CuK\(\alpha\) (wave length is \( \lambda = 1.542 \) Å) were used. X-ray diffraction patterns were taken at room temperature in an angular range of 5°-120°. The magnetic and galvanomagnetic properties were measured at the Atomistitut, TU Wien using an MPMS XL7 (Quantum Design) SQUID magnetometer. The magnetic properties were measured in magnetic fields of up to 10 kOe in the temperatures range 150-330 K. The Hall Effect were measured by the standard dc four-probe method for the temperature 4.2 K and in magnetic fields of up to 100 kOe.

3. Results and discussion

The STT were determined from the temperature dependences of the magnetization and electrical resistance using the method of tangens \[9, 10\], according to which this temperatures were determined at their intersection (table 1). It is obvious that for all alloys doping with germanium, the STT is lower than in the original ternary compound \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{14} \), and the temperatures decrease as the germanium content in the alloy increases. The only exception is the alloy \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{13}\text{Ge}_1 \), which is demonstrates STT superior to those for the original alloy. In aluminium doping alloys a completely different tendency can be traced, the STT, on the contrary, exceed to those for the alloy \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{14} \), and increase as the aluminium content increases.

| Alloy              | \( A_s \) | \( A_f \) | \( M_s \) | \( M_f \) | \( e/a \) | \( n^*\cdot10^{23}, 1/\text{cm}^3 \) |
|-------------------|----------|----------|----------|----------|---------|--------------------------|
| \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{11}\text{Ge}_3 \) | 207      | 214      | 202      | 197      | 8.19    | 0.13                     |
| \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{12}\text{Ge}_2 \) | 218      | 224      | 216      | 209      | 8.20    | 0.43                     |
| \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{13}\text{Ge}_1 \) | 205      | 246      | 237      | 212      | 8.21    | 0.18                     |
| \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{14} \)         | 231      | 238      | 232      | 225      | 8.22    | 0.48                     |
| \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{13}\text{Al}_1 \) | 237      | 240      | 234      | 229      | 8.20    | 0.21                     |
| \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{12}\text{Al}_2 \) | 264      | 273      | 264      | 258      | 8.18    | 0.07                     |
| \( \text{Ni}_{50}\text{Mn}_{36}\text{Sb}_{10}\text{Al}_4 \) | 282      | 306      | 300      | 274      | 8.14    | 0.19                     |

The calculation of \( e/a \) was carried out according to the equation (1) below \[11\] as the sum of the products of the number of valence d- and s-electrons of the chemical element including in the alloy, on the fraction of this chemical element:

\[
\frac{e}{a} = (C_d \cdot Z_d) + (C_n \cdot Z_n) + (C_p \cdot Z_p),
\]
where $C_A$, $C_B$, $C_D$ – concentrations of elements A, B, D; $Z_A$, $Z_B$, $Z_D$ – the number of external (valence) electrons for the elements A, B, D. The number of valence electrons was assumed to be 10, 7, 5, 4 and 3 for Ni (3d$^8$4s$^2$), Mn (3d$^6$4s$^1$), Sb (5s$^2$5p$^3$), Ge (4s$^2$4p$^2$) and Al (3s$^2$3p$^1$), respectively.

For alloys containing germanium, it was found that lowering ratio $e/a$ leads to a decrease in STT. In alloys containing aluminium, the situation is completely opposite: with decreasing $e/a$ STT increases, although between them there should be a direct relationship. It should be noted that the Ni$_{50}$Mn$_{36}$Sb$_{12}$Ge$_2$ and Ni$_{50}$Mn$_{36}$Sb$_{13}$Al$_1$ alloys have the same value of e/a, but their STT differs significantly. Thus, it becomes obvious that the ratio e/a is not sufficient to describe the behavior of STT, especially in four-component systems, a similar conclusion was made in [12].

The results of x-ray studies of the Ni$_{50}$Mn$_{36}$Sb$_{12}$Ge$_2$ alloy are shown in figure 1. It can be seen that the sample is single-phase (all reflections correspond to the same structural type), i.e., the sample contains 100% compound with the Ni$_2$MnSb-type (the lattice parameters is $a = 5.957$ Å). Other alloys contain an irrelevant small amount of secondary phases: Ni$_{50}$Mn$_{36}$Sb$_{14}$ alloy sample contain 1.9 wt %Ni$_2$Sb, Ni$_{50}$Mn$_{36}$Sb$_{12}$Al$_2$ alloy sample contain 10.3 wt % MnAl and 1.3 wt % Ni$_3$Sb. Since the content of the secondary phases is insignificant, in the present work it was assumed that all alloys are in the austenitic state. From the x-ray studies $V_{\text{cell}}$ was determined. As an example, table 2 shows the values of the $V_{\text{cell}}$ for some of the studied alloys. It was found that a decrease in the $V_{\text{cell}}$ does not lead to an increase in STT, on the contrary, they decreases. It was expected that the alloy Ni$_{50}$Mn$_{36}$Sb$_{12}$Ge$_2$ will show the highest values of STT, since it has the lowest value of $V_{\text{cell}} = 211.29$ Å$^3$. The highest STT values are characteristic for alloy Ni$_{50}$Mn$_{36}$Sb$_{12}$Al$_2$ despite the fact that the $V_{\text{cell}}$ for this alloy is 212.35 Å$^3$.

Table 2. Values of the $V_{\text{cell}}$ and density of valence electrons n for the alloys Ni$_{50}$Mn$_{36}$Sb$_{14}$Z$_x$ (Z = Al, Ge; x = 0; 2).

| Alloy            | $V_{\text{cell}}$, Å$^3$ | n, 1/cm$^3$ |
|------------------|---------------------------|-------------|
| Ni$_{50}$Mn$_{36}$Sb$_{12}$Ge$_2$ | 211.29                    | 62.09 · 10$^{22}$ |
| Ni$_{50}$Mn$_{36}$Sb$_{14}$      | 213.95                    | 61.47 · 10$^{22}$ |
| Ni$_{50}$Mn$_{36}$Sb$_{12}$Al$_2$| 212.35                    | 61.63 · 10$^{22}$ |

In addition, the definition of $V_{\text{cell}}$ can be complicated by the fact that the structural transformation in the alloy has not yet been completed, and therefore the phase composition is represented by a mixture of martensite and austenite. It becomes obvious that the $V_{\text{cell}}$ as well as the ratio e/a cannot reliably describe the behavior of STT.

In accordance with the above, varying the density of valence electrons $n$ can be considered as a way to influence STT. This approach was implemented in [13] for alloys of the Ni-Mn-Ga system, the density of valence electrons was calculated with equation (2):
where \( n_1 \) is the average number of atoms per unit cell (for alloys of the systems Ni-Mn-Z \((Z = \text{Ga, In, Sb, Sn})\) it is 16).

It was assumed, that as the parameter \( n \) increases, the STT should also increase, but this does not occur in the studied alloys. For the alloys Ni\(_{50}\)Mn\(_{36}\)Sb\(_{14}\) and Ni\(_{50}\)Mn\(_{36}\)Sb\(_{12}\)Al\(_2\) difference between the values of the parameter \( n \) is not significant: 61.47 \( \times \) 10\(^{22} \) 1/cm\(^3\) and 61.63 \( \times \) 10\(^{22} \) 1/cm\(^3\), respectively. However, the STT values for these alloys are differ significantly from each other. For example, the \( M_s \) (start temperature of martensitic transformation) for alloy Ni\(_{50}\)Mn\(_{36}\)Sb\(_{14}\) equal to 232 K, and for alloy Ni\(_{50}\)Mn\(_{36}\)Sb\(_{12}\)Al\(_2\) – 264 K. Alloy Ni\(_{50}\)Mn\(_{36}\)Sb\(_{12}\)Ge\(_{2}\) has the lowest values of STT, despite parameter \( n \) is 62.09 \( \times \) 10\(^{22} \) 1/cm\(^3\).

Thus, the correlation between the STT and the above mentioned parameters \((c/a, V_{cell}, n)\) is not always fulfilled. Since during structural transformations, a change in the electronic structure also occurs, one can try to find a correlation between the parameters of the electronic subsystem and the STT. One of such parameters is the concentration of charge carriers, determined, e.g., from the Hall Effect measurements.

The field dependences of the Hall resistivity \( \rho_H(H) \) and the magnetization curves (obtained at 4.2 K) have the same general view. The curves \( \rho_H(H) \) and \( M(H) \) have two distinguishable intervals of magnetic fields, such as the technical magnetization region \((H < 10 \text{ kOe})\), and the paraprocess region at higher fields. Taking into account the fact that for \( \rho_H(H) \) and \( M(H) \) curves there are no saturation effect and linear dependence even in strong magnetic fields, we used the approach proposed in [14]. The coefficients \( R_\text{NHE} \) and \( R_\text{AHE} \) were determined from the dependences \( \rho_H(H) \) and \( M(H) \) in the paraprocess region with the equation (3):

\[
\frac{\rho_H}{H} = R_\text{NHE} + \frac{4\pi R_\text{AHE}M}{H},
\]

where \( R_\text{NHE} = R_\text{AHE} \), \( N \) – demagnetization factor. The first term in equation (3) describes the normal Hall Effect (NHE), which in metals is caused by the Lorentz force on the charge carriers and is proportional to the applied magnetic field. The second term in equation (3) is determined by so-called anomalous Hall Effect (AHE).

From the figure 2 it can be seen that equation (3) is valid for \( \rho_H(H) \) and \( M(H) \) of all investigated alloys in the limit of strong magnetic fields \((H > 10 \text{ kOe})\).

The NHE coefficient \( R_\text{NHE} \) is characterized by the number \( n^* \) of current (charge) carriers per unit specimen volume with equation (4):

\[
R_\text{NHE} = \frac{1}{n^* c},
\]

where \( c \) is the light velocity, \( e \) is the charge of a current carrier. In the present work for Ni\(_{50}\)Mn\(_{36}\)Sb\(_{14-x}\)Z\(_{x}\) \((Z = \text{Al, Ge}; x = 0; 1; 2; 3; 4)\) alloys the coefficient of the NHE was determined and then the number of charge carriers \( n^* \) was calculated, obtained values are given in table 1. In all cases the coefficient of NHE is positive, therefore, in the studied alloys the main charge carriers are holes.

It should be noted that the Fermi surface of Heusler alloys has a complex topology and contains the various sheets of both electronic and hole types. Therefore, to accurately determine the concentration of current carriers, it is necessary to have the data on Fermi surface topology of certain alloy, as well as the data on the mobility of charge carriers belonging to certain sheets of the Fermi surface. This is quite a challenge. However, as shown in [15-20], estimating the concentration of current carriers using one band model makes it possible to qualitatively track the changes in the electronic characteristics.
and qualitatively determine the correlation between them even in such complex compounds. Therefore, we also use one band model.

Figure 2. Dependences $\rho_{H}/H$ on $M/H$ for alloys Ni$_{50}$Mn$_{36}$Sb$_{14}$-$x$Z$_{x}$ ($Z = \text{Al, Ge}; x = 0; 1; 2; 3; 4$).

Figure 3 shows the dependences STT on $n^*$ for all investigated alloys. It is obvious that aluminium-doped alloys exhibit higher STT values compared to the initial ternary compound Ni$_{50}$Mn$_{36}$Sb$_{14}$. Germanium-doped alloys, on the contrary, demonstrate lower STT than the initial compound. This fact is especially pronounced for $A_s$ and $M_f$. Temperatures $M_s$ and $A_f$ for alloys doped by 1 at.% of Al or Ge and Ni$_{50}$Mn$_{36}$Sb$_{14}$ are almost the same. Probably the reason for this is a small amount of alloying element. Alloy Ni$_{50}$Mn$_{36}$Sb$_{14}$ has the highest value of $n^*$ equal to $4.8 \times 10^{23}$ 1/cm$^3$.

Values of $n^*$ for alloys doped by 1; 2 and 4 at% of Al is $2.1 \times 10^{23}$; $7 \times 10^{22}$; $1.9 \times 10^{23}$ 1/cm$^3$, respectively. $M_s$ for alloy Ni$_{50}$Mn$_{36}$Sb$_{14}$ is 232 K, for alloy Ni$_{50}$Mn$_{36}$Sb$_{13}$Al$_1$ – 234 K. In the future this tendency will continue, e.g., as $n^*$ decreases values of $M_s$ will increase: for alloy Ni$_{50}$Mn$_{36}$Sb$_{10}$Al$_4$ $M_s$ is 300 K. The value of $n^*$ was expected to be higher than 300 K, but it is 264 K. It is obviously that this dependence is not continue, a similar situation is also observed for $M_f$, $A_s$ and $A_f$. For the alloys doped by Ge, in general, a different trend is observed: as $n^*$ decreases values of $M_s$ will decrease too, more exactly, for alloy Ni$_{50}$Mn$_{36}$Sb$_{13}$Ge$_2$ $M_s = 216$ K, for alloy Ni$_{50}$Mn$_{36}$Sb$_{11}$Ge$_3$ – 202 K. The exception is the alloy Ni$_{50}$Mn$_{36}$Sb$_{13}$Ge$_{1}$ for which $n^*$ = $0.18 \times 10^{23}$ 1/cm$^3$ and $M_s$ = 237 K.

It should be noted that alloys Ni$_{50}$Mn$_{36}$Sb$_{14}$ and Ni$_{50}$Mn$_{36}$Sb$_{13}$Ge$_2$ have approximately the same values of $n^*$: $4.8 \times 10^{23}$ and $4.3 \times 10^{23}$ 1/cm$^3$, but $M_s$ for this alloys is differ: 232 and 216 K, respectively. Values of $n^*$ for alloys Ni$_{50}$Mn$_{36}$Sb$_{10}$Al$_4$ and Ni$_{50}$Mn$_{36}$Sb$_{13}$Ge$_1$ are also close in meaning ($0.19 \times 10^{23}$; $0.18 \times 10^{23}$ 1/cm$^3$), however values of $M_s$ for this alloys are significantly differ in meaning: 300 and 237 K, respectively.
Figure 3. Dependence STT on charge carrier concentration: ▲ - Ni$_{50}$Mn$_{36}$Sb$_{14}$, ◆ - Ni$_{50}$Mn$_{36}$Sb$_{13}$Al$_{1}$, ■ - Ni$_{50}$Mn$_{36}$Sb$_{12}$Al$_{2}$, □ - Ni$_{50}$Mn$_{36}$Sb$_{10}$Al$_{4}$, ○ - Ni$_{50}$Mn$_{36}$Sb$_{13}$Ge$_{1}$, Δ - Ni$_{50}$Mn$_{36}$Sb$_{12}$Ge$_{2}$, ● - Ni$_{50}$Mn$_{36}$Sb$_{11}$Ge$_{3}$. The horizontal line passes through temperatures corresponding to the initial ternary compound Ni$_{50}$Mn$_{36}$Sb$_{14}$.

4. Conclusions
The magnetization, the electrical resistivity and the Hall Effect of Ni$_{50}$Mn$_{36}$Sb$_{14-x}$Z$_{x}$ (Z = Al, Ge; x = 0; 1; 2; 3; 4) Heusler alloys were measured at temperatures from 150 K to 330 K and in magnetic fields of up to 10 kOe. The $V_{cell}$, the $e/a$ parameter, the density of valence electrons $n$, and the charge carriers concentration $n^{*}$ were determined. An attempt to find a correlation between STT and above mentioned parameters were made. It was shown that this correlation is not strongly, there is only a general trade.

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