

Theoretical Modeling of Magnetocaloric Effect in Heusler Ni-Mn-In Alloy by Monte Carlo Study

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Abstract. In this paper we present a theoretical model for calculation of the (positive and negative) magnetocaloric effects and magnetic properties of the Heusler $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy by the classical Monte Carlo study. By the help of the proposed model the temperature dependences of the magnetization, tetragonal deformation, heat capacity, positive and negative isothermal magnetic entropy changes for magnetic field variation are obtained. All quantities are in good qualitative agreement with the available experimental data.

Introduction

The magnetic cooling technology is based on the ability of any magnetic material to change its temperature and entropy under the influence of a magnetic field [1]. Such effect is called the magnetocaloric effect (MCE). Recent experimental researches have shown a presence of the large MCE in $\text{Gd}_5(\text{Si}_2\text{Ge}_2)$, $\text{MnFeP}_{1-x}\text{As}_x$ and $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ alloys [1]. The reason of large MCE in these alloys is the coupled magnetostructural (MS) transition. In these alloys an applied magnetic field causes the alignment of magnetic moments under adiabatic conditions. Due to this alignment the magnetic part of the total entropy is reduced. In order to compensate this reduction, other components of the total entropy (electronic and lattice parts) are increased. It leads to heating of alloys (the positive MCE). However, there are certain materials where the applied magnetic field leads to further spin disorder, causing an increase in the magnetic part and a decrease in the electronic and lattice parts of the total entropy. In that case the compounds are cooling (the negative MCE). In these materials the 1st order magnetic transition from antiferromagnetic (AF) state to ferromagnetic (FM) one takes place (e.g. $\text{Fe}_{0.49}\text{Rh}_{0.51}$ [2]).

Recent experimental researches have shown the possibility of using of Heusler Ni-Mn-X (X = In, Sn, Sb) alloys as refrigerants in the technology of magnetic cooling. [3]. In these compounds two types of large MCE (positive and negative) are observed experimentally. The reason of the positive MCE in these alloys is following. Recent *ab initio* simulations of $\text{Ni}_{50}\text{Mn}_{25+x}\text{X}_{25-x}$ for a martensite and austenite phases clearly have shown the competition of AF and FM interactions in both states. The AF interaction is the interaction between of the excess of Mn_2 atoms occupying the X sublattice sites and Mn_1 atoms on the Mn sublattice sites i.e. $\text{Mn}_1\text{-Mn}_2$ and $\text{Mn}_2\text{-Mn}_2$ interactions. At the same time both austenitic and martensitic phases also have the following ferromagnetic interactions: $\text{Mn}_1\text{-Mn}_1$, $\text{Mn}_1\text{-Ni}$ and $\text{Mn}_2\text{-Ni}$ [4]. This fact leads to complex phase transitions with decreasing temperature such as the cubic paramagnetic \rightarrow cubic FM transition near Curie temperature T_C and cubic FM \rightarrow mixed tetragonal AF-FM transition near the structural transition temperature T_m . The negative MCE occurs at coupled MS transition from the mixed AF-FM martensite to the FM austenite and the positive MCE takes place at magnetic phase transition from the FM austenite to the PM austenite after application of the magnetic field [5].

In this work we theoretically investigate the (positive and negative) MCE of the Heusler $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy by the Monte Carlo simulations.

Theoretical Model

In our model we use a three-dimensional lattice with periodic boundary conditions and with real unit cells of Heusler Ni-Mn-X alloys. The first unit cell may be considered as four interpenetrating fcc sublattices with the atom of Mn at site $(1/2, 1/2, 1/2)$, the atom of Ga at site $(0, 0, 0)$ and atoms of Ni at sites $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$, respectively (Fig. 1a). This unit cell corresponds to the high-temperature parent cubic austenite in which the lattice distortions (compression or expansion) are absent along the x , y and z axes. During cooling the austenite transforms to the low-temperature tetragonal martensite with tetragonal unit cell (Fig. 1b). The martensitic phase may exhibit several low-temperature variants and in our model we consider two variants of martensite with the lattice deformation along $\pm x$ axes. So in the case of the austenite we consider all interactions between nearest-neighbor atoms within cubic unit cell (Fig. 1a) and in the case of the martensite we propose interactions between nearest atoms within tetragonal unit cell (Fig. 1b).

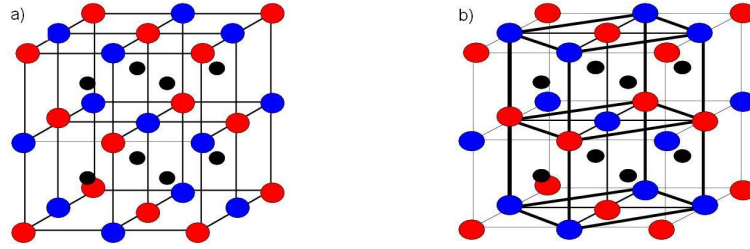


Fig. 1: (Color online) Left panel: The cubic $L2_1$ structure of the Heusler Ni_2MnIn alloy. Right panel: The tetragonal bct ($c/a=0.94$) structure of Ni_2MnIn . Here blue, red and black symbols are Mn, In and Ni atoms, respectively. Black bold solid line indicates the tetragonal unit cell.

In the proposed model for formation of $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy the excess of the Mn_2 atoms is taken as corresponding to nominal compositions whereas configuration of the Mn_2 atoms in the In sublattice is set randomly. Crystallographic sites of the lattice occupied by Mn_1 , Mn_2 and Ni atoms are ascribed with magnetic and structural degree of freedom whereas ones occupied by In atoms having only structural degree of freedom. The magnetic subsystem is describes by a mixed q -state Potts model for FM-PM phase transition [4]. Here q is the number of spin states. Since the Ni-Mn interaction in Ni-Mn-X alloy plays important role in the making of ferromagnetism we should take into account spin magnetic moments S of the Mn and Ni atoms. The spin magnetic moments S of the Mn and Ni atoms are different and for Mn atoms S is $4/2$ and therefore 5 spin projections are possible and hence $q_{\text{Mn}}=5$, opposite the Ni atoms have $S=1$ with following 3 spin projections and $q_{\text{Ni}}=3$. Therefore in our model we consider the model with three - five spin states Potts model. The structural subsystem is described by a degenerated three state Blume-Emery-Griffiths (BEG) model for structural transformations from the austenite to the martensite [4].

The generalized Hamiltonian (Eq. 1) consists of three parts: magnetic part (Eq. 2), elastic part (Eq. 3) and the magnetoelastic interaction (Eq. 4) [4].

$$H = H_m + H_{el} + H_{int}, \quad (1)$$

$$H_m = - \sum_{\langle i,j \rangle}^{NN} J_{i,j}^m \delta_{S_i, S_j} - g\mu_B H_{ext} \sum_i \delta_{S_i, S_g}, \quad (2)$$

$$H_{el} = -(J + U_1 g\mu_B H_{ext} \sum_i \sigma_g \sigma_j) \sum_{\langle i,j \rangle}^{NN} \sigma_i \sigma_j - K \sum_{\langle i,j \rangle}^{NN} (1 - \sigma_i^2)(1 - \sigma_j^2) - k_B T \ln(p)(1 - \sigma_i^2), \quad (3)$$

$$H_{int} = 2 \sum_{\langle i,j \rangle}^{NN} U_{i,j} \delta_{S_i, S_j} \left(\frac{1}{2} - \sigma_i^2 \right) \left(\frac{1}{2} - \sigma_j^2 \right) - \frac{1}{2} \sum_{\langle i,j \rangle}^{NN} U_{i,j} \delta_{S_i, S_j} , \quad (4)$$

Here $J_{i,j}^m$ is the exchange constant of the magnetic subsystem, J and K are the exchange constants of the structural subsystem, $U_{i,j}$ and U_1 are the magnetoelastic interaction constants, T is the temperature, H_{ext} is the external magnetic field, δ_{S_i, S_j} is the Kronecker symbol which restricts spin-spin interactions to the interactions between the same q states, S_i is a spin defined on the lattice site $i=1, \dots, N$, S_g is a *ghost spin*, whose direction is determined by the external magnetic field (positive H_{ext} favors spins parallel to the ghost spin), k_B is the Boltzmann constant, μ_B is the Bohr's magneton, g is the Lande factor, p is the degeneracy factor, $\sigma_i = 1, 0, -1$ represents the deformation state of each site of the lattice ($\sigma_i = 0$ corresponds to the undistorted state whereas $\sigma_i = \pm 1$ represents distorted states), σ_g is a *ghost deformation* state, whose value is that of a structural variant in the external magnetic field (positive H_{ext} favors deformation states coinciding with the ghost deformation state). Summing up is taken over all nearest neighbor pairs.

In the elastic part of the Hamiltonian (Eq. 3) the first term describes the interaction between single strains σ_i in the tetragonal (martensitic) state. The second term shows the favorable orientation dependence of the martensitic variant in the external magnetic field. The third term defines the interaction between single strains σ_i in the cubic (austenitic) phase. The last term characterizes a temperature-dependent crystal field [4].

In the proposed model the temperature dependencies of a magnetization and a strain order parameter (Eq. 5), a specific heat and entropy of a system (Eq. 6) are presented by:

$$m = \frac{1}{N} \left(\frac{q_{Ni} N_{max}^i - N_{Ni}}{q_i - 1} + \frac{q_{Mn} N_{max}^{Mn} - N_{Mn}}{q_{Mn} - 1} \right), \quad \varepsilon = \frac{1}{N} \sum_i \sigma_i , \quad (5)$$

$$C(T, H_{ext}) = \frac{\langle H^2 \rangle - \langle H \rangle^2}{k_B T^2}, \quad S(T, H_{ext}) = \int_{T_1}^{T_2} \frac{C(T, H_{ext})}{T} dT . \quad (6)$$

Where N is the total number of Ni and Mn atoms, q_{Ni} and q_{Mn} are the numbers of magnetic states of Ni and Mn atoms, N_{max}^{Ni} and N_{max}^{Mn} are the maximal numbers of identical magnetic states on the lattice, N_{Ni} and N_{Mn} are the numbers of Ni and Mn atoms on the lattice, respectively. For $\varepsilon = 0$ in the DBEG model we have the cubic state. In the case of $\varepsilon = 1$ the martensitic state for one of variants with $\sigma_i=1$ or $\sigma_i=-1$ takes place.

Numerical Results

In this section we present the numerical results of our model for description of the MCE of the $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy using Monte Carlo simulation techniques [4]. The simulation was carried out using following Metropolis algorithm: (1) Generate the initial spin configuration (the ferromagnetically ordered state) and the initial strain configuration (the tetragonal state, one of the martensitic variants). (2) Choice the equilibrium strain configuration on the lattice with tetragonal or cubic unit cell. (2.1) Randomly select a particular site i of the lattice: if $\sigma_i=1$ or $\sigma_i=-1$ then calculate the initial elastic energy H_{1el} (Eq. 3) on the tetragonal unit cell; if $\sigma_i=0$ then calculate the initial elastic energy H_{1el} (Eq. 3) on the cubic unit cell. (2.2) Randomly change the values of the strain σ_i on this particular site i and calculate the energy for this new configuration H_{2el} : if $\sigma_i=1$ or $\sigma_i=-1$ then calculate the initial elastic energy H_{2el} (Eq. 3) on the tetragonal unit cell; if $\sigma_i=0$ then calculate the initial elastic energy H_{2el} (Eq. 3) on the cubic unit cell. (2.3) If $H_{2el} < H_{1el}$, accept the new configuration with energy H_{2el} and go to step (3). (2.4) If $H_{2el} > H_{1el}$, calculate the probability factor $\exp(-\Delta H_{el}/k_B T)$: generate a random number r such that $0 < r < 1$; if $r < \exp(-\Delta H_{el}/k_B T)$, accept the

new configuration with energy H_{2el} , else preserve the old configuration of strain and return to step (3). (3) Choice the equilibrium spin configuration on the lattice with selected unit cell. (3.1) Calculate of the full energy with the selected values of the strain on the particular site i : if $\sigma_i=1$ or $\sigma_i=-1$ then calculate the initial full energy H_1 (Eq. 1) on tetragonal unit cell; if $\sigma_i=0$ then calculate the initial full energy H_1 (Eq. 1) on the cubic unit cell. (3.2) Randomly change the values of the spin state q on this particular site i and calculate the energy for this new configuration H_2 : if $\sigma_i=1$ or $\sigma_i=-1$ then calculate the initial full energy H_2 (Eq. 1) on tetragonal unit cell; if $\sigma_i=0$ then calculate the initial full energy H_2 (Eq. 1) on the cubic unit cell. (3.3) If $H_2 < H_1$, accept the new configuration with energy H_2 and go to step (4). (3.4) If $H_2 > H_1$, calculate the probability factor $\exp(-\Delta H/k_B T)$: generate a random number r such that $0 < r < 1$; if $r < \exp(-\Delta H/k_B T)$, accept the new configuration with energy H_2 , else preserve the old configuration of spin and return to step (2.1). (4) Move the next site of the lattice (2.1). (5) Repeat the entire process until all the lattice sites are swept.

Since we have used real lattice, the coordination number of nearest-neighbor atoms has taken various values for each atom of the cubic and tetragonal unit cells. For the case of magnetic subsystem in the martensitic state each Mn atom has 8 nearest-neighbor Mn₁, 2 Mn₂, and 8 Ni atoms, each Ni atom has 4 nearest-neighbor Mn₁ and Mn₂ atoms; in the austenitic state each Mn atom has 12 Mn₁, 6 Mn₂, 8 Ni atoms and each Ni atom has 4 nearest-neighbor Mn₁ and Mn₂ atoms. For the case of the structural subsystem in the martensitic state each atom Mn₁ (In or Mn₂) has 8 Mn₁ (In or Mn₂) atoms, 2 In or Mn₂ (Mn₁) atoms and 8 Ni atoms, respectively, and each Ni atom has 4 Mn₁, In or Mn₂ atoms and 6 nearest Ni atoms; in the austenitic state each atom Mn₁ (In or Mn₂) has 12 nearest Mn₁ (In or Mn₂) atoms, 6 nearest In or Mn₂ (Mn₁) atoms and 8 Ni atoms, respectively, and each Ni atom has 4 Mn₁, In or Mn₂ atoms and 6 nearest Ni atoms. In our simulations we have used the lattice in which 1098 Mn₁, 396 Mn₂, 1728 Ni and 703 In atoms, respectively. As the time unit, we used one Monte Carlo step consisting of N attempts to change q_{Ni} , q_{Mn} and σ_i variables. For a given temperature, number of the Monte Carlo steps on each site was taken 5×10^5 . The simulation started from the ferromagnetic martensitic phase. The internal energy of the system H and the order parameters m and ε were averaged over 400 configurations for each 100 Monte Carlo steps. In order to obtain equilibrium values of H , m and ε , the first 10^4 Monte Carlo steps were discarded. The degeneracy factor p and the Lande factor g were taken as $p = 2$ and $g = 2$. The value of dimensionless magnetoelastic interaction $U_1 = -1.5$ has been chosen that the magnetic and structural transitions are coinciding in an external magnetic field. The magnitude of spin states (i.e. the q_{Ni} and q_{Mn} variable) were taken as corresponding to a random number r such that $0 < r < 1$ and fix the values of q_{Ni} and q_{Mn} according to the scheme: if $0 \leq r \leq 1/3$ then $q_{Ni} = l$, $l = 1 \dots 3$ and $0 \leq r \leq 1/5$ then $q_{Mn} = l$, $l = 1 \dots 5$.

For the calculation of MCE in the Ni₅₀Mn₃₄In₁₆ alloy, the following values of constants were used (Table 1).

Table 1: Model parameters in [meV] for Ni₅₀Mn₃₄In₁₆ alloy.

	J	$J_{Mn_1-Mn_1}^m$	$J_{Mn_1-Mn_2}^m$	$J_{Mn_2-Mn_2}^m$	$J_{Mn_1-Ni}^m$	$J_{Mn_2-Ni}^m$	U	K
<i>Martensite</i>	3.06	0.258	-17.5	-0.82	4.59	3.02	12.24	0.765
<i>Austenite</i>	3.06	-0.83	-5.74	-1.48	3.18	2.82	7.65	0.765

The values of magnetic austenitic and martensitic exchange constants for Ni₅₀Mn₃₄In₁₆ alloy have been taken from results of *ab initio* simulations [4]. The value of the structural exchange interaction J has been obtained from Monte Carlo simulations taking into account the experimental temperature of the MS transition T_{ms} and reduced modeled temperature of the MS transition T_{ms}^* from the following relation $J = k_B T_{ms} / T_{ms}^*$. This value of J is equal approximately with experimental exchange constant $J \sim 2$ meV for Ni-Mn-Ga, which obtained from experimental data of the phonon dispersion curves of the Ni-Mn-Ga [6].

Results of our Monte Carlo simulations of the magnetic and magnetocaloric properties of $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy are presented in Figures 2 – 4.

In Figure 2 we present theoretical and experimental results of temperature dependencies of the magnetization and strain order parameter for $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy in magnetic fields of 0 and 5 T. Thermodynamic temperature T will be able to calculate from the expression for the reduced temperature $T^* = k_B T / J$ using value of $J = 3.06$ meV (Table 1). We observe here two phase transitions at 305 K ($T_C^* \sim 8.5$) and at 215 K ($T_{ms}^* \sim 6.05$), respectively. At $T_C^* \sim 8.5$ we find the PM-FM transition in cubic (austenitic) state. The second transition is the magnetostructural transition from the FM cubic state to the mixed AF-FM tetragonal phase. The behavior of the strain order parameter ε shows the onset of the structural phase deformation at 215 K ($T_{ms}^* \sim 6.05$). The experimental temperature dependence of magnetization was taken from Ref. [5].

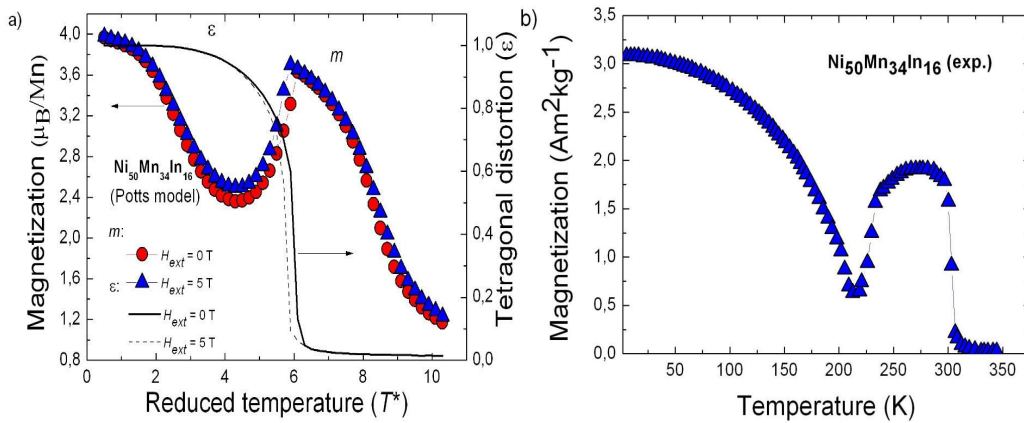


Fig. 2: (Color online) Left panel: The theoretical temperature dependencies of magnetizations curves and strain deformations of $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy in magnetic fields of 0 and 5 T. Here, filled circles and the line are results obtained for zero magnetic field and filled triangle symbols, dash line are simulations in magnetic field of 5 T. Right panel: The experimental magnetization curve of $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy in magnetic field of 5 mT.

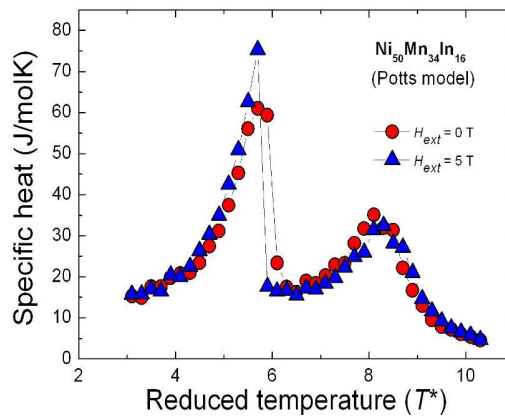


Fig. 3: (Color online): Theoretical temperature dependencies of the specific heat of $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy in magnetic fields of 0 and 5 T.

As can we see from Fig. 3 there are two picks (at $T_C^* \sim 8.5$ and $T_{ms}^* \sim 6.05$) on temperature dependencies of the specific heat, which correspond to the PM-FM transition in cubic state and the MS transition from the FM cubic state to the mixed AF-FM tetragonal phase. The external magnetic field shifts the MS transition temperature T_{ms}^* in a low-temperature region and the Curie temperature in a high-temperature region T_C^* , respectively.

Fig. 4 presents theoretical and experimental isothermal magnetic entropy changes in $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy upon variation of the magnetic field from 0 to 5 T. Here we find the positive MCE at the FM-PM transition temperature (near the room temperature) and the negative MCE at

the coupled MS phase transition temperature. For decreasing of a discrepancy between the values of the theoretical and experimental positive MCE it should be to carry out more accurate simulation (e.g. an increase in the number of the Monte Carlo steps but this increase leads to a rise of the computer computation time). The experimental result for ΔS_{mag} has been obtained from isothermal magnetization measurements with the help of the Maxwell relation and was taken from Ref. [5].

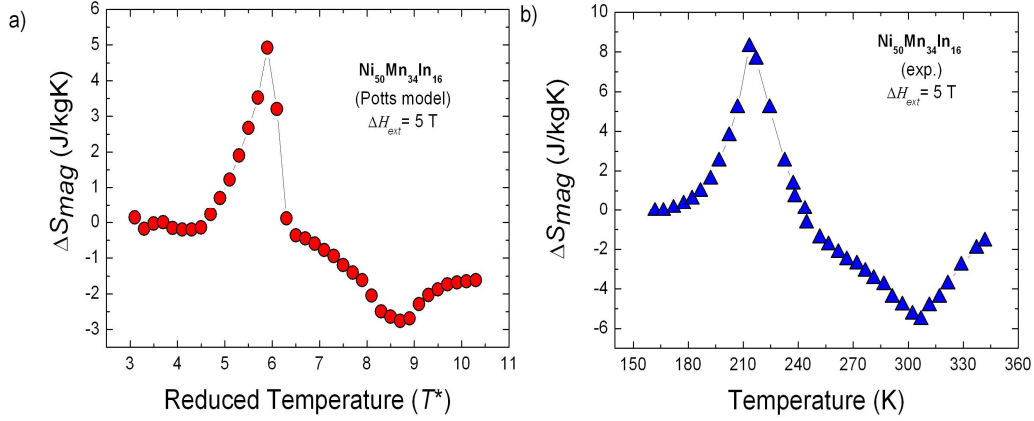


Fig. 4: (Color online): Theoretical (left panel) and experimental (right panel) ΔS_{mag} in $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy at magnetic field of 5 T.

Summary

In this work the magnetic properties and the positive and negative MCE of $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy upon various variation of the magnetic field from 0 to 5 T have been studied by the Monte Carlo simulations. It is shown that the results of the calculations are in good qualitative agreement with available experimental data. The magnetic subsystem is described by the q-state Potts model. For the structural subsystem, we have used the Blume-Emery-Griffiths model. Using the *ab initio* competitive ferro-antiferromagnetic exchange constants and the change-over the magnetic and structural interactions from the tetragonal to the cubic real unit cell of Heusler alloys have allowed us to obtain the complex phase transitions with decreasing temperature such as the austenite PM - FM and austenite FM \rightarrow mixed martensite AF-FM and to calculate the MCE at both phase transition temperatures. It is significant that the Heisenberg Hamiltonian with using the *ab initio* exchange integrals and real unit cell of $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ alloy do not reproduce that complex trend of phase transitions [4]. In spite of that we can determine exactly the Curie temperature of Heusler alloys by the help both Potts model and Heisenberg one using the *ab initio* integrals and real unit cell.

Acknowledgements

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