Theoretical model of the coupled magnetostructural phase transitions in Heusler Ni-Mn-In alloys by Monte Carlo simulation

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Abstract. On the basis of classical Monte Carlo simulations, we investigate the temperature and magnetic field dependencies of magnetization, strain order parameter, specific heat and entropy of Ni-Mn-In Heusler alloy, in which the part of the Mn atoms interact antiferromagnetically. It is shown that this antiferromagnetic exchange is responsible for existence of several magnetic phase transitions in the Heusler alloys. It is shown that with the help of the model Hamiltonian we obtain coupled magnetostructural phase transition. Results of simulations are in good qualitatively agreement with the experimental data.

1. Introduction

In recent years, Ni-Mn-X (X =In, Sn, Sb) alloys has been attracting attention in view of their unique properties, such as the shape memory effect, the magnetocaloric effect (MCE), the magneto resistance and other properties are associated with the martensitic transition [1, 2]. These properties are applicable in developing actuator materials and materials for magnetic refrigeration.

Recent experiments have shown that in Heusler Ni-Mn-X alloys, the structural phase transition from the paramagnetic (PM) high-temperature cubic (austenitic) phase to the ferromagnetic (FM) low-temperature tetragonal (martensitic) phase can occur [1]. It is well known from experimental studies and ab initio simulations, that in stoichiometric Ni₅₀Mn₂₅X₂₅ alloys all Mn atoms on its regular sublattice site interact FM. However, on non-stoichiometric Ni₅₀Mn₂₅₋ₓXₓ alloys revealed, the excess of Mn₂ atoms occupying the sites of X atoms, interact with each other and with Mn₁ atoms on the Mn sublattice sites antiferromagnetically (AF) [1-3]. Therefore, this fact leads to complex phase transitions with decreasing temperature such as the cubic PM → FM transition at Curie temperature T_C and the magnetostructural (MS) cubic FM → mixed tetragonal AF-FM transition (MST) at the structural transition temperature T_m. The experimental studies have shown that two types of MCE can occur in Ni-Mn-X alloys. The negative MCE occurs at the temperature of the coupled MST and the positive MCE takes place at the Curie temperature after application of the magnetic field [2].

In this work we theoretically investigate the magnetic and magnetocaloric properties at the coupled MS transition in Heusler Ni-Mn-In compound.
2. 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 In 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 [4]. This unit cell corresponds to the high- temperature parent cubic austenite without the lattice distortions along the x, y and z axes. During cooling the austenite transforms to the low-temperature tetragonal martensite with tetragonal unit cell [4]. The martensitic phase may exhibit several low-temperature variants and in our model we consider two variants of martensite with the lattice deformation along ±x or ±y or ±z axes. So, in the case of the austenite we consider all interactions between nearest-neighbor atoms within cubic unit cell and in the case of the martensite we propose interactions between nearest atoms within tetragonal unit cell [4].

In the proposed model for formation of Ni_{50}Mn_{34}In_{16} alloy the configuration of excess of Mn^2 atoms in the In sublattice is set randomly. Crystallographic sites of the lattice occupied by Mn^2, Mn^1 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 described by a mixed q-state Potts model for FM-PM phase transition [3]. 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 here we consider the 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 [3].

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

$$H = H_m + H_e + H_{int},$$  \hspace{1cm} (1)

$$H_m = -\sum_{\alpha,\beta} J_{ij}^{\alpha\beta} \delta_{S_i,S_j} - g\mu_B H_{ext} \sum_i \delta_{S_i,0},$$  \hspace{1cm} (2)

$$H_e = -(J + U_i g\mu_B H_{ext} \sum_i \delta_{S_i,0}) \sum_{\alpha,\beta} \sigma_{i,\alpha} \sigma_{j,\beta} - K \sum_{\alpha,\beta} \sum_{\alpha',\beta'} (1 - \sigma_{i,\alpha}^2) (1 - \sigma_{j,\beta}^2) - k_B T \ln(p)(1-\sigma_i^2),$$  \hspace{1cm} (3)

$$H_{int} = 2 \sum_{\alpha,\beta} U_{ij} \delta_{S_i,\alpha} \delta_{S_j,\beta} \left( \frac{1}{2} - \sigma_i^2 \right) \left( \frac{1}{2} - \sigma_j^2 \right) - \frac{1}{2} \sum_{\alpha,\beta} U_{ij} \delta_{S_i,\alpha} \delta_{S_j,\beta}.$$  \hspace{1cm} (4)

Here $J_{ij}^{\alpha\beta}$ is the exchange constant of the magnetic subsystem, $J$ and $K$ are the exchange constants of the structural subsystem, $U_{ij}$ and $U_i$ are the magnetoelastic interaction constants, $T$ is the temperature, $H_{ext}$ is the external magnetic field, $\delta_{S_i,0}$ 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 $i=1,..,N$, $S_g$ is a ghost spin, whose direction is determined by the external magnetic field, $\delta_{S_i,\alpha}$ is the degeneracy factor, $\sigma_i$ 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 proposed model the temperature dependencies of a magnetization and a strain order parameter (5), a specific heat and entropy of a system (6) are presented by:

$$m = \frac{1}{N} \left( q_{\text{Ni}} N_{\text{Ni}}^{\text{max}} - N_{\text{Ni}} + q_{\text{Mn}} N_{\text{Mn}}^{\text{max}} - N_{\text{Mn}} \right) / q_{\text{Ni}} - 1,$$  \hspace{1cm} (5)

$$\varepsilon = \frac{1}{N} \sum_i \sigma_i,$$  \hspace{1cm} (6)

$$C(T,H_{\text{int}}) = \frac{<H^2> - <H^2>_0}{k_B T^2},$$  \hspace{1cm} (7)

$$S(T,H_{\text{int}}) = \int_{T_1}^T \frac{C(T,H_{\text{int}})}{T} dT.$$  \hspace{1cm} (8)
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, \( \Delta N_{Ni}^{max} \) and \( \Delta N_{Mn}^{max} \) 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 BEG model we have the cubic state. For \( \varepsilon = 1 \), we find the martensite for one of variants with \( \sigma_{i} = 1 \) or \( \sigma_{i} = -1 \).

3. Numerical results

In this section we solve numerically the model for description of the magnetic properties of the Ni\(_{50}\)Mn\(_{34}\)In\(_{16}\) alloy using Monte Carlo simulation techniques [3]. The simulation was carried out using standard Metropolis algorithm. Changes in the independent variables \( q_{Ni}, q_{Mn} \) and \( \sigma_{i} \) are accepted or rejected on tetragonal and cubic unit cells according to a single-site transition probability \( W = \min\{1, \exp(-\Delta H/k_{B}T)\} \). 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. So, for example, for Mn\(_{1}\) atoms we have considered the first-nearest Ni atoms, the second-nearest Mn\(_{2}\) or In atoms and the third-nearest Mn\(_{1}\) atoms, respectively. For the case of the Ni atoms we have taken into account the first-nearest Mn\(_{1}\) and Mn\(_{2}\) or In atoms and the second-nearest Ni atoms, respectively. In our simulations we have used the lattice in 1098 Mn\(_{1}\), 396 Mn\(_{2}\), 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 \( \sigma_{i} \) variables. For a given temperature, number of the Monte Carlo steps on each site was taken \( 5 \times 10^5 \). The simulation started from the ferromagnetic martensitic phase. The internal energy of the system \( H \) and the order parameters \( m \) and \( \varepsilon \) were averaged over 400 configurations for each 100 Monte Carlo steps. In order to obtain equilibrium values of \( H, m \) and \( \varepsilon \), the first \( 10^5 \) 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 \( 0 \leq r \leq l/3 \) then \( q_{Ni} = l \), \( l = 1...3 \) and \( 0 \leq r \leq l/5 \) then \( q_{Mn} = l \), \( l = 1...5 \).

In our simulations we have used the following values of the model constants (Table 1).

| \( J \) | \( J_{Mn-Mn}^{m} \) | \( J_{Mn-Ni}^{m} \) | \( J_{Ni-Ni}^{m} \) | \( J_{Mn-Ni}^{1} \) | \( J_{Mn-Ni}^{2} \) | \( U_{m} \) | \( K \) |
|---|---|---|---|---|---|---|---|
| Martensite | 3.06 | 0.258 | -17.5 | -0.82 | 4.59 | 3.02 | 12.24 | 0.765 |
| Austenite | 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 Ni\(_{50}\)Mn\(_{34}\)In\(_{16}\) alloy have been taken from results of \textit{ab initio} simulations [3]. 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 MST \( T^*_{ms} \) from relation \( J = k_{B}T_{ms}/T^*_{ms} \).

In Figure 1a we present theoretical magnetization curves of Ni\(_{50}\)Mn\(_{34}\)In\(_{16}\) alloy in magnetic fields of 0 and 5 T. Figure 1b shows the experimental data of magnetizations for Ni\(_{50}\)Mn\(_{34}\)In\(_{16}\) alloy in magnetic fields of 5 mT and 5 T (See the Inset), respectively [2]. 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 \( (T^*=8.5) \) and at 215 K \( (T^*=6.05) \), respectively. At \( T^*<8.5 \) we find the PM-FM transition in an austenite. The second transition is the MST from the FM cubic state to the mixed AF-FM martensite. The behavior of the strain order parameter \( \varepsilon \) shows the onset of the structural phase deformation at 215 K \( (T^*=6.05) \).

Figure 2 presents theoretical and experimental isothermal magnetic entropy changes in Ni\(_{50}\)Mn\(_{34}\)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 MST temperature. It should be noted that for better similarity between behaviors of theoretical and experimental MCE curves and quantitative agreement between the modeling values of MCE and experimental ones it is needed to carry out more accurate simulation (e.g. an increase in the
number of the Monte Carlo steps and the lattice size, but this increase leads to a rise of the computer computation time). The experimental result for $\Delta S_{\text{mag}}$ has been obtained from isothermal magnetization measurements with the help of the Maxwell relation and was taken from Ref. [2].

![Figure 1a](image1.png) ![Figure 1b](image2.png)

Figure 1a. (Color online): The theoretical thermomagnetizations curves and strain deformations of Ni$_{50}$Mn$_{34}$In$_{16}$ alloy. Here, filled circles and the line are results in zero magnetic field and triangle symbols, dash line are simulations in magnetic field of 5 T.

Figure 1b. (Color online): The experimental magnetization curves of Ni$_{50}$Mn$_{34}$In$_{16}$ alloy in an external magnetic field [2]. Here filled (blue) triangles are data in magnetic field of 5 mT and filled (red) circles are data in magnetic field of 5 T (See the Inset).

![Figure 2a](image3.png) ![Figure 2b](image4.png)

Figure 2a. (Color online): Theoretical $\Delta S_{\text{mag}}$ in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy upon variation of the magnetic field from 0 to 5 T.

Figure 2b. (Color online): Experimental $\Delta S_{\text{mag}}$ in Ni$_{50}$Mn$_{34}$In$_{16}$ alloy upon variation of the magnetic field from 0 to 5 T [2].

Summary
In this work the magnetic properties and the positive and negative MCE of Ni$_{50}$Mn$_{34}$In$_{16}$ alloy upon variation of the magnetic field from 0 to 5 T have been studied by the Monte Carlo simulations using ab initio magnetic exchange constants and real unit cell of Heusler alloys. It is shown that the results of the calculations are in good qualitative agreement with available experimental data.

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