Monte Carlo study of magnetocaloric properties of Ni-Mn-Ga Heusler alloys

V Buchelnikov¹, V Sokolovskiy¹, S Taskaev¹, V Khovaylo² and P Entel³

¹Department of Condensed Matter Physics, Chelyabinsk State University, Chelyabinsk 454001, Russia
²Institute of Radioengineering and Electronics of Russian Academy of Sciences, Moscow 125009, Russia
³Department of Physics and Center for Nanointegration, CENIDE, University of Duisburg-Essen, Duisburg 47048, Germany
buche@csu.ru

Abstract. A three-dimensional Monte Carlo model has been used for theoretical description of magnetic and magnetocaloric properties of Ni₂.18Mn₀.82Ga Heusler alloys undergoing first order magnetostructural phase transition. For this alloy, calculated temperature dependence of magnetization, magnetic contribution to the total specific heat and magnetic entropy change $\Delta S_{mag}$ are in good qualitatively agreement with available experimental data.

1. Introduction
Recent researches have shown that Ni-Mn-Ga Heusler alloys have received significant attention with respect to their magnetocaloric properties [1]. These alloys have approximately the same values of magnetocaloric effect (MCE) as the best MCE alloys, such as Gd-Si-Ge, Mn-As-Sb, La-Fe-Si.

Stoichiometric Ni₂MnGa alloy undergoes a martensitic transformation on cooling below $T_m \sim 200$ K. Ferromagnetic ordering sets in at sufficiently higher temperature, $T_C \sim 376$ K. Recent experimental studies of non-stoichiometric Ni$_{2+x}$Mn$_{1-x}$Ga have revealed that both the transition temperatures are sensitive to the chemical composition and with an increase of Ni excess $x T_m$ increases whereas $T_C$ shows a tendency to decrease [2]. Both the structural and magnetic transitions are merged at the range of compositions $0.18 < x < 0.27$. For these alloys, a large MCE at the point of first order magnetostructural phase transition (MST) has been reported [3].

In this work we study theoretically coupled MST, MCE and magnetic properties of the Ni$_{2.18}$Mn$_{0.82}$Ga Heusler alloy by means of a classical Monte Carlo method.

2. Theoretical model
In our model we use a three-dimensional lattice with periodic boundary conditions and with real unit cells of Ni-Mn-Ga Heusler alloys. The first unit cell may be considered as four interpenetrating fcc sublattices with Mn at site $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Ga at site $(0, 0, 0)$ and Ni at sites $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$, respectively [4]. This unit cell corresponds to the high-temperature parent cubic austenite. During cooling, the austenite transforms to the low-temperature tetragonal martensite with tetragonal unit cell...
The martensitic phase may exhibit several variants and in our model we consider two variants of martensite with the lattice deformation along ±x axis.

There are two types of Ni atoms (Ni_A and Ni_B) in the Ni_{12.5}Mn_{16.5}Ga alloys. The Ni_A atoms are in regular Ni atom’s positions and the Ni_B atoms are occupying regular Mn atom’s positions. Recent ab initio calculations of magnetic exchange integrals of Ni-Mn-Ga have shown that the Ni_A-Mn magnetic exchange interaction is positive and the largest of all exchange integrals (Mn-Mn, Ni_A-Mn, Ni_B-Mn, respectively) and this exchange interaction guarantees a ferromagnetic phase. The results of ab initio calculations of tetragonal phases (c/a=0.94) for Ni_{12.5}Mn_{16.5}Ga alloys have shown that the second-nearest Mn atoms that are located in (a, b) plane interact antiferromagnetically (AF).

In the proposed model, the configuration of excess of Ni_B atoms in the Mn sublattice for formation of Ni_{12.5}Mn_{16.5}Ga alloy is set randomly. Crystallographic sites of the lattice occupied by Mn, Ni_A and Ni_B atoms are associated with both magnetic and structural degrees of freedom whereas ones occupied by Ga atoms have only structural degree of freedom. As is known, the spin magnetic moments S of the Mn and Ni atoms are different. The Mn atom has S=3/2 and therefore q_{Mn}=5 spin projections or states are possible, opposite to Ni with S=1 with q_{Ni}=3 spin states. So the magnetic subsystem describes a three - five spin states Potts model allowing to simulate the ferro-paramagnetic phase transition [6]. The structural subsystem is described by a degenerated three state Blume-Emery-Griffiths (BEG) model for structural transformations from austenite to martensite [5, 6].

The generalized Hamiltonian (1) includes three parts: the magnetic part (2), the elastic part (3) and the magnetoelastic interaction (4) [6].

\[
H = H_m + H_e + H_{int}, \tag{1}
\]

\[
H_m = -\sum_{i,j} J_{ij}^{m} \delta_{S_i, S_j} - g\mu_B H_{ext} \sum_i \delta_{S_i, S_0}, \tag{2}
\]

\[
H_e = -\left(J + U_1 g\mu_B H_{ext} \sum_i \delta_{S_i, S_0} - K \sum_{i,j} \left(1 - \sigma_i^j\right)\left(1 - \sigma_j^i\right) - k_B T \ln(p)\left(1 - \sigma_i^j\right)\right), \tag{3}
\]

\[
H_{int} = 2 \sum_{i,j} \delta_{S_i, S_j} \left(1/2 - \sigma_i^j\right)\left(1/2 - \sigma_j^i\right) - 1/2 \sum_{i,j} U_{i,j} \delta_{S_i, S_j}. \tag{4}
\]

Here J_{ij}^{m} is the exchange constant of the magnetic subsystem, J and K are the structural exchange constants for tetragonal and cubic states, respectively, U_{i,j} and U_{i} are the magnetoelastic interaction constants, T is the temperature, H_{ext} is the external magnetic field, \delta_{S_i, S_j} is the Kronecker symbol which restricts spin-spin interactions to the interactions between the same q_{Mn} states for Mn atoms and q_{Ni} states for Ni atoms, S_i is a spin defined on the lattice site \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 are distorted states), \sigma_i is a ghost deformation state, whose value is that of a structural variant in the external magnetic field. Sums are taken over neighbor pairs in the first, second and third Mn coordination sphere and in the first and second coordination sphere for Ni atoms.

With respect to the elastic part of the Hamiltonian (Eq. 3), the first term describes the interaction between single strains \sigma_i in the tetragonal state. The second term characterizes the favorable orientation dependence of the martensitic variant in the external magnetic field. The third term defines the interaction between single strains \sigma_i in the cubic phase, and the parameter K characterizes the martensitic transition. The last term characterizes a temperature-dependent crystal field [5].

The magnetization, the strain order parameter, the specific heat and entropy of the system we define as:

\[
m = \frac{1}{N} \left(\frac{q_{Ni} N_{max}^{Ni} - N_{Ni}}{q_{Ni} - 1} + \frac{q_{Mn} N_{max}^{Mn} - N_{Mn}}{q_{Mn} - 1}\right), \quad \sigma = \frac{1}{N} \sum_i \sigma_i, \tag{5}
\]

\[
c(T, H_{ext}) = \frac{< H^2 > - < H >^2}{k_B T^2}, \quad S(T, H_{ext}) = \frac{1}{T} \int c(T, H_{ext}) dT. \tag{6}
\]
Here $N$ 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, $\Lambda_{Ni_{max}}$ and $\Lambda_{Mn_{max}}$ 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 $\epsilon = 0$ in the BEG model, we have the cubic state. For $\epsilon=1$, we find the martensite for one of variants with $\sigma_l=1$ or $\sigma_l=-1$.

3. Numerical results

In this section we present the numerical results of our model for the Ni$_{2.18}$Mn$_{0.82}$Ga alloy using Monte Carlo simulation techniques. The simulation was carried out using standard Metropolis algorithm [6]. Since we have used the real crystal lattice, the coordination number of neighbor atoms has various values for each atom of the cubic and tetragonal unit cells. So, we have taken into account neighbor pairs in the first, second and third coordination sphere for the Mn atoms and in the first and second coordination sphere for Ni atoms. In our simulations we have used the lattice with 900 Mn, 1728 Ni, 198 Ni$_3$ and 1099 Ga atoms, respectively. As time unit, we used one Monte Carlo step consisting of $N$ attempts to change $q_{Ni}$, $q_{Mn}$ and $\sigma_l$ variables. For a given temperature, the 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 $\epsilon$ were averaged over 400 configurations for each 100 Monte Carlo steps. In order to obtain equilibrium values of $H$, $m$ and $\epsilon$, 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 $U_1 = 0.25$ has been chosen such 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 $0 < r < 1$ fixing the values of $q_{Ni}$ and $q_{Mn}$ according to the scheme: if $0 < r < l/3$ then $q_{Ni} = l, l = 1...3$ and $0 < r < l/5$ then $q_{Mn} = l, l = 1...5$.

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

| Table 1. Model parameters in meV for Ni$_{2.18}$Mn$_{0.82}$Ga alloy |
|-----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Martensite            | 2.0             | 1.45            | 4.57            | 0.04            | -3.9            | 12              | 0.56            |
| Austenite             | 2.0             | 0.4             | 4.64            | 0.02            | 0               | 2               | 0.56            |

The values of magnetic austenitic and martensitic exchange constants we have been taken from $ab$ initio simulations of exchange magnetic integrals of Ni$_{2.25}$Mn$_{0.75}$Ga alloy [6]. The information about the approximate value of the structural exchange interaction was taken from experimental data of the phonon-dispersion curves of Ni-Mn-Ga alloys [7]. According to Ref. [5, 7] the exchange constant $J$ is proportional to the energy of the soft phonon and for a Ni-Mn-Ga alloy with $T_m \sim 284$ K and $T_c \sim 364$ K the value of $J$ at $T_m$ is $\sim 2$ meV. In our model we have taken the value of $J = 2$ meV. The values of $U_{mart}$, $U_{aust}$ and $K$ were chosen to allow for fixed ferromagnetic exchange constants to satisfy experimentally observed condition of coinciding magnetic and structural phase transitions.

Figure 1 presents the theoretical magnetization, tetragonal distortion and specific heat as a functions of the reduced temperature $T = k_B T / J_{Mn-Ni}$ for the Ni$_{2.18}$Mn$_{0.82}$Ga alloy. As can be seen from Figure 1a, the curves of $m$ and $\epsilon$ coincide in the phase transition region which points to a coupled nature of the MST. As is obvious from Figure 1b, our theoretical value of the zero-field specific heat change at MST for Ni$_{2.18}$Mn$_{0.82}$Ga alloy is $\sim 100$ J/mol K. This value compares well with experimental data ($\sim 145$ J/mol K) for Ni$_{2.18}$Mn$_{0.82}$Ga alloy [8].

In Figure 2 we present the magnetic entropy change $\Delta S_{mag}$ of Ni$_{2.18}$Mn$_{0.82}$Ga upon variation of the magnetic field from 0 to 5 T. The experimental result for $\Delta S_{mag}$ has been obtained from isothermal magnetization measurements with the help of the Maxwell relation [3]. The discrepancy between the peak value of $\Delta S_{mag}$ calculated by the Monte Carlo method and that determined from the Maxwell relation can be due to a limited applicability of the Maxwell relation to the materials undergoing first order magnetic phase transitions [9].
Figure 1a. (Color online): The theoretical thermomagnetization curves and strain deformations of Ni$_{2.18}$Mn$_{0.82}$Ga. Here, circles and the line are results for zero magnetic field and triangle symbols, dashed line are simulations for a magnetic field of 5 T.

Figure 1b. (Color online): The theoretical specific heat curves of Ni$_{2.18}$Mn$_{0.82}$Ga. Here, the line with squares is the result in zero magnetic field and the line with circles is the result in a magnetic field of 5 T.

Figure 2a. (Color online): Theoretical $\Delta S_{\text{mag}}$ for Ni$_{2.18}$Mn$_{0.82}$Ga upon variation of the magnetic field from 0 to 5 T.

Figure 2b. (Color online): Experimental $\Delta S_{\text{mag}}$ Ni$_{2.18}$Mn$_{0.82}$Ga upon variation of the magnetic field from 0 to 5 T.

Summary

In this work the magnetic properties and the MCE of Ni$_{2.18}$Mn$_{0.82}$Ga in varying magnetic field from 0 to 5 T have been studied by Monte Carlo simulations using ab initio magnetic exchange constants and a realistic unit cell of Heusler alloys. It is shown that the results of the calculations are in good qualitative agreement with available experimental data.

Acknowledgments

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