Monte Carlo modeling of exchange bias effect in Ni$_{50}$Mn$_{25+x}$Sb$_{25-x}$ Heusler alloys

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Abstract. A theoretical model for investigation of an exchange bias effect in Heusler Ni$_{50}$Mn$_{25+x}$Sb$_{25-x}$ alloys by Monte Carlo simulations is presented. It is shown that the exchange bias effect of Heusler Ni$_{50}$Mn$_{25+x}$Sb$_{25-x}$ alloys is observed in the composition range $7.5 < x < 15$ at the temperature $T = 13$ K. For case of Ni$_{50}$Mn$_{37.5}$Sb$_{12.5}$ alloy, we have obtained the exchange bias field $H_{EB} = 0.05$ T at 4.6 K and a blocking temperature $T_B = 46.7$ K. Theoretical results are in good qualitatively agreement with experimental data.

1. Introduction
The Heusler Ni-Mn-X (X = In, Sn, Sb) alloys have the unique properties, such as the shape memory effect, the giant inverse and direct magnetocaloric effect, the large magnetoresistence, the exchange bias effect and others interesting magnetic properties which are associated with the martensitic transition [1-7]. These properties are applicable in developing actuator materials, spintronic and magnetic cooling technology.

When a ferromagnet (FM) is in contact with an antiferromagnet (AFM) a shift of a hysteresis loop along a magnetic-field axis can occur which is called the exchange bias effect (EB). Usually, this shift of the hysteresis loop is observed after cooling an entire system in an external magnetic field below the Neel temperature $T_N$ of the AFM. Though this effect has been well known for many years [8, 9] its microscopic origin is still discussed. Recent experiments have shown that in Heusler Ni-Mn-X alloys the EB is experimentally observed [5, 6]. An origin of the EB is next. When the temperature changes, a structural phase transition from a paramagnetic (PM) cubic (austenitic) phase to the FM tetragonal (martensitic) phase can occur in Heusler Ni-Mn-X alloys [1-7]. It is well known, that in stoichiometric Ni$_{50}$Mn$_{25}$X$_{25}$ alloys all Mn$_1$ atoms on its regular sublattice sites interact FM (figure 1). However, recent experiments of non-stoichiometric Ni$_{50}$Mn$_{25+x}$X$_{25-x}$ alloys have revealed that in the martensite, the excess of Mn$_2$ atoms occupying the sites of X atoms, interact with Mn$_1$ atoms AFM (figure 2) [2, 3, 7]. Thus, in the martensitic state of Ni$_{50}$Mn$_{25+x}$X$_{25-x}$ alloys the FM and AFM interactions are coexisted. Opposite, there is the FM interaction between all Mn atoms only in the austenitic state. It should be note, the presence of AFM interactions in the martensitic phase are responsible for the EB.

2. The theoretical model
In the proposed model we use a simple three-dimensional cubic lattice with periodic boundary conditions and take into account the magnetic interactions only in two coordination spheres. Since the magnetic moment of the Ni atoms ($\approx 0.3 \mu_B$) are small compared to the Mn magnetic moment ($\approx 4.0$
µB) and since the Sb atoms have not spin moment, we omit contributions to the magnetic interaction from the Ni and Sb atoms altogether. The Sb atoms are treated as nonmagnetic inclusions at lattice sites. Since the Ni concentration is constant in Ni\(^{50}\)Mn\(^{25+}\)\(_x\)Sb\(^{25-}\)_\(_x\) alloys we do not take into account the Ni lattice sites. For the case of stoichiometric Ni\(^{50}\)Mn\(^{25}\)Sb\(^{25}\) alloy, the concentrations of Mn\(_1\) and Sb atoms on the model lattice are taken as 50%. For the case of non-stoichiometric Ni\(^{50}\)Mn\(^{25+}\)\(_x\)Sb\(^{25-}\)_\(_x\) alloy the Mn\(_2\) excess are located randomly at the Sb sites on the model lattice and the concentration of Mn\(_2\) atoms is determined from the experimental compositions. So, in the proposed model, we consider FM and AFM Heisenberg’s spin interactions with anisotropy term using \textit{ab initio} exchange constants.

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The generalized Hamiltonian (1) includes the FM part (2) and the AFM one (3) and the interaction between FM and AFM parts (4).

\[
H = H_\text{FM} + H_\text{AFM} + H_\text{FM-AFM}^*
\]

\[
H_\text{FM} = -J_\text{FM1} \sum_{\langle i,j \rangle \in \text{FM}_1} S_i S_j - J_\text{FM2} \sum_{\langle i,j \rangle \in \text{FM}_2} S_i S_j - \sum_{i \in \text{FM}} \left( K_\text{FM} S_i^2 + \mu_B g H S_i \right).
\]

\[
H_\text{AFM} = -J_\text{AFM1} \sum_{\langle i,j \rangle \in \text{AFM}_1} S_i S_j - J_\text{AFM2} \sum_{\langle i,j \rangle \in \text{AFM}_2} S_i S_j - \sum_{j \in \text{AFM}} \left( K_\text{AFM} S_j^2 + \mu_B g H S_j \right).
\]

\[
H_\text{FM-AFM} = -J_\text{int1} \sum_{\langle i \in \text{FM} \cap \text{AFM}, j \in \text{FM} \cap \text{AFM} \rangle} S_i S_j - J_\text{int2} \sum_{\langle i \in \text{FM} \cap \text{AFM}, j \in \text{FM} \cap \text{AFM} \rangle} S_i S_j.
\]

Here, \(J_{\text{FM1}}, J_{\text{FM2}}, J_{\text{AFM1}}, J_{\text{AFM2}}\) and \(J_{\text{int1}}, J_{\text{int2}}\) are the FM and AFM exchange constants in the first and second coordination spheres; \(S\) is the three-dimensional vector of unit length; \(K_{\text{FM}}\) and \(K_{\text{AFM}}\) are the magnetic anisotropy terms for Mn\(_1\) and Mn\(_2\) atoms, respectively; \(H\) is the external magnetic field; \(g\) is the Lande factor; \(\mu_B\) is the Bohr’s magneton; \(J_{\text{int1}}\) and \(J_{\text{int2}}\) are the magnetic exchange constants between Mn\(_1\) and Mn\(_2\) atoms in the first and second coordination spheres. Sums are performed over all nearest neighbor and next nearest neighbor pairs.

In the proposed model we use renormalized parameters defined by ration over \(J_{\text{FM1}}\): \(A^* = A/J_{\text{FM1}}\), here \(A = J_{\text{FM2}}, J_{\text{AFM1}}, J_{\text{AFM2}}, K_{\text{FM}}, K_{\text{AFM}}, J_{\text{int1}}, J_{\text{int2}}\). The reduced temperature defines as

\[\frac{T}{T_\text{Curie}} = \frac{\beta}{K_{\text{FM}}} \frac{\mu_B^2 g^2 H^2}{K_{\text{FM}}},\]

where \(T_{\text{Curie}}\) is the Curie temperature.

**Figure 1.** Stoichiometric Ni\(^{50}\)Mn\(^{25}\)Sb\(^{25}\) alloys.

**Figure 2.** Non-stoichiometric Ni\(^{50}\)Mn\(^{25+}\)\(_x\)Sb\(^{25-}\)_\(_x\) alloys.
$T^* = \frac{k_B T}{J_{FM_i}}$,  \hspace{1cm} (5)

where $k_B$ is the Boltzmann constant.

The total normalized magnetization of the system can be presented as

$$m = m_{FM} + m_{AFM} = \frac{1}{N} \sqrt{\sum_i S_{ix}^2 + \sum_i S_{iy}^2 + \sum_i S_{iz}^2}.$$

Here, $m_{FM}$ and $m_{AFM}$ are normalized magnetizations of Mn$_1$ and Mn$_2$ atoms respectively; $x$ denotes Mn$_1$ and Mn$_2$ atoms.

The exchange bias field defines as

$$H_{eb} = \frac{(H_+ - H_-)}{2},$$

where $H_+$ and $H_-$ are those fields of the hysteresis loop branches for increasing and decreasing field, where normalized magnetization becomes zero.

3. Model parameters

The corresponding simulations have been carried out using the standard Metropolis algorithm [10]. The changes in the spin states $S_i$ ($S_{ix}$, $S_{iy}$, $S_{iz}$) are treated independently and accepted or rejected according to the single-site transition probability $W = \min\{1, \exp[-\Delta H^*/T]\}$. For simulations of the cubic lattice we used six near neighbors and twelve next nearest neighbors for the first and second coordination spheres, respectively. The number of the lattice sites was equal to $N = L^3$, where $L = 15$. The time unit is one Monte Carlo step, which consist of $N$ attempts to change the $S_i$ variables. For a given temperature number of the Monte Carlo steps on each site is $10^5$. We start the Monte Carlo simulations from the ordered state at low temperature. For the case of Mn$_1$ atoms, the spin variables are $S_{ix} = 0$, $S_{iy} = 0$, $S_{iz} = 1$, and for the case of Mn$_2$ atoms the spin variables are $S_{ix} = 0$, $S_{iy} = 0$, $S_{iz} = -1$, respectively. The various quantities are averaged over 400 configurations taken every 100 Monte Carlo steps and discarding the first $10^4$ Monte Carlo steps for equilibrium. The Lande factor was taken $g = 2$. In our simulations we used the fixed magnetic constants obtained from ab initio calculations for Ni$_{50}$Mn$_{37.5}$Sb$_{12.5}$ alloy (figure 3 and table 1) but magnetic anisotropy constants have varied.

![Figure 3. The magnetic exchange constants for Ni$_{50}$Mn$_{37.5}$Sb$_{12.5}$ alloy as a function of the distance $d/a$ between pair atoms $i$ and $j$ obtained from ab initio calculations.](image-url)
Table 1. Magnetic exchange constants for Ni$_{50}$Mn$_{37.5}$Sb$_{12.5}$ alloy.

| Exchange constants (meV) | 1$^{st}$ coord. sphere | 2$^{nd}$ coord. sphere |
|-------------------------|------------------------|-----------------------|
| $J_{FM}$                | 2                      | 1                     |
| $J_{AFM}$               | -1                     | -1                    |
| $J_{int}$               | -2                     | -2                    |

4. Numerical results
In this section we solve numerically our model by using Monte Carlo techniques. For all simulations we have used the exchange constants which list in Table 1 and the magnetic anisotropy terms $K_{FM} = 0.05$ meV and $K_{AFM} = 0.015$ meV.

At figure 4 the theoretical magnetic field dependences of the normalized magnetization $m$ for ferromagnetic and antiferromagnetic components are shown. In the figure is clearly observable a shift of the hysteresis loops aside the positive field. Corresponding EB field for Ni$_{50}$Mn$_{37.5}$Sb$_{12.5}$ alloy is equal to $H_{EB} = 0.05$ T. Figure 5 presents the hysteresis loops of non-stoichiometric Ni$_{50}$Mn$_{25+x}$X$_{25-x}$ alloys ($x = 5, 7.5, 7.75, 8, 9, 10, 12.5$) at $T = 13$ K. As we can see, the hysteresis loops become broader and higher with increasing of concentration $x$. It is obvious because with bigger concentration we will have more excess Mn atoms and as a result bigger value of magnetization.

Figure 4. Theoretical ferromagnetic and antiferromagnetic hysteresis loops of Ni$_{50}$Mn$_{37.5}$Sb$_{12.5}$ alloy at $T = 4.6$ K.

Figure 5. Theoretical hysteresis loops of Ni$_{50}$Mn$_{25+x}$X$_{25-x}$ alloys at $T = 11.6$ K.

Figure 6. Experimental temperature–concentration ($T$-$x$) phase diagram of Ni$_{50}$Mn$_{25+x}$X$_{25-x}$ alloys [6].

Figure 7. Theoretical concentration dependence of EB of Ni$_{50}$Mn$_{25+x}$X$_{25-x}$ alloys at $T = 13$ K.
As it is well known, the EB in Ni-Mn-Sb alloys exists only in the narrow range of excess Mn atoms (7.5 < x < 15). It can be seen from the experimental phase diagram (see figure 6) [6].

At figure 7 we present a theoretical concentration dependence of the EB for the Ni_{50}Mn_{37.5}Sb_{12.5} alloys at T = 13 K. From this figure we can see that the EB exists in the concentration range from x = 7.5 until x = 15. Some authors [11] explain this effect by the following way. At high concentration (amount of excess Mn\textsubscript{2} atoms) an exchange interaction between spins of FM and AFM atoms lost, and as a result lead to a decreasing of Curie temperature and corresponding disappearing of EB. On the other hand, because of the non-magnetic atoms involve in domain formation, the increasing of its amount (low concentration of excess Mn\textsubscript{2} atoms) lead to a decreasing of EB effect. The calculated behavior of the EB is in a good agreement with the experimental data.

Figure 8 presents the theoretical dependences of EB field and the coercive field \(H_C\) from the temperature for Ni_{50}Mn_{37.5}Sb_{12.5} alloy. In agreement with experiments [5, 12, 13] (see Figure 9) the EB field and the coercive field \(H_C\) decrease with temperature almost linearly going to zero at the temperature \(T_B\). \(T_B\) is called the blocking temperature. It is important to note that \(T_B\) is not equal to the Neel temperature of the AFM, which equal \(T_N = 62.4 \text{ K}\) in our simulations. There are several reasons for this effect which have been clearly described in the paper [11].

5. Conclusions
In this work we have investigated exchange bias effect in the Heusler Ni-Mn-Sb alloys by classical Monte Carlo simulations. In the proposed model we have used a simple cubic lattice with periodic boundary conditions and take into account the magnetic interactions only in two coordination spheres. The whole lattice consists of magnetic atoms and non-magnetic impurities. We have considered the ferromagnetic and antiferromagnetic Heisenberg’s spin interactions with anisotropy term using \textit{ab initio} exchange constants. Configuration of antiferromagnetic atoms sets at non-magnetic sites of the lattice randomly.

Our simulations have shown that the exchange bias field depends on a concentration of the antiferromagnetic atoms, the temperature and number of hysteresis loops. Moreover the value of the bias field decreasing with increasing temperature and for Ni_{50}Mn_{37.5}Sb_{12.5} alloy we have found a temperature of blocking of the exchange bias effect. Theoretical blocking temperature is close to experimental value.
6. Acknowledgments
This work was supported by grants RFBR Grant 10-02-92110, President of Russian Federation Grant MK-1891.2010.2 and Grant of support for young scientists OSPO 2010. We had further support by the SPP 1239 of the German Science Foundation (DFG).

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