First-principles and Monte Carlo studies of C-doped Ni$_{45}$Co$_5$Mn$_{37}$In$_{13}$ Heusler alloys

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Abstract. In this work, we report the study of the effect of carbon on electronic and magnetic properties of the Ni$_{43}$Co$_{46}$Sn$_{11}$Cx (x = 0, 2, 4, 8) alloys. They have been studied the MCE and mechanical properties of carbon-doped Ni$_{43}$Co$_{46}$Sn$_{11}$Cx (x = 0, 2, 4, 8) alloys. They have been shown that $T_m$ temperatures increase with carbon increasing. Besides, the largest magnetic entropy change, $\Delta S_m$ of 34.6 J/(kgK), has been observed for compound with x = 2 for a field change of 5 T.

1 Introduction

In recent years, Ni-Mn-Z (Z = sp element) alloys have gained increasing interest for their potential application as multifunctional materials because of their diverse properties, which include the ferromagnetic shape memory effect, magnetocaloric effect (MCE), large magneto-resistance and exchange bias effect [1-5]. In general, the physical properties of Heusler alloys with different chemical composition are related to the strong coupling between a complex magnetism and a crystal lattice. Moreover, due to the different atomic configuration the competing ferromagnetic (FM), ferrimagnetic (FIM) and antiferromagnetic (AFM) orders can be expected in the ortho-spinoidal alloys because of Rudermann-Kittel-Kasuya-Yoshida (RKKY)-type exchange interactions between Mn atoms [6, 7]. As the result, in the majority of Ni-Mn-Z alloys the high-temperature austenitic phase is FM with a high magnetization while the low-temperature martensitic phase is FIM or AFM with a low magnetization. We note that the largest AFM coupling is found between Mn$_{1y}$ and Mn$_{2y}$ atoms located in tetragonal crystal. Here, Mn$_{1y}$ are Mn atoms occupying a regular Mn sublattice while Mn$_{2y}$ are excess Mn atoms substituted for Z atoms.

Among extensive researches on ternary and quaternary Ni-Mn-Z and Ni-Y-Mn-Z (Y = 3d element), there were few reports on the substitution of C in these alloys [8-10]. The modifying Mn$_{1y}$-Mn$_{2y}$ distance can be expected caused by doping C element. Hence, because of the smaller ionic radius of C, the decrease of the cell volume would result in the decrease of the Mn$_{1y}$-Mn$_{2y}$ distance, and as a consequence, tune both the martensitic transformation temperature ($T_m$) and the Curie temperatures of austenite ($T_c^A$) and martensite ($T_c^M$). The effect of the carbon on the martensitic transformation of Ni-Mn-Ga Heusler alloys has been discussed by Lu et al. [8] and Chen et al. [9]. In both studies the substitution of 1.6 at.% C for Ga content was found to increase the $T_m$ temperature and to disappear the intermartensitic transformation from five-layer modulated martensite to non-modulated martensite. Recently, Zhang et al. [10] studied the MCE and mechanical properties of carbon-doped Ni$_{43}$Mn$_{46}$Sn$_{11}$Cx (x = 0, 2, 4, 8) alloys. They have shown that $T_m$ temperatures increase with carbon increasing. Besides, the largest magnetic entropy change, $\Delta S_m$ of 34.6 J/(kgK), has been observed for compound with x = 2 for a field change of 5 T.

In the current study, in order to extend our knowledge as a carbon influence on properties of Ni-Co-Mn-In alloys, we use first-principles and Monte Carlo (MC) calculations to investigate their electronic and magnetic properties in dependence on different substitutions of C for In and Mn$_{1y}$ atoms.

2 Ab initio details and results

To perform the electronic structure calculations, we have used the spin-polarized relativistic Korringa-Kohn-Rostoker (SPRKKR) band structure code [11] in conjunction to the Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) to the exchange-correlation potential [12]. The calculation of the magnetic exchange couplings, magnetic moments, and density of states (DOS) curves for C-doped NiCoMnIn alloys have been carried out for the austenitic L2$_1$ structure (space group $Fm\overline{3}m$) and for the martensitic L1$_2$ structure (space group $Fm\overline{m}m$). We have used the

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MATEC Web of Conferences 33, 05004 (2015)
DOI: 10.1051/matecconf/20153305004
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lattice constants and tetragonal ratio, $c/a$, from the energy relaxation calculations performed for supercell approach. We have taken into account two compositions with substitution of 5% C for In and for Mn$_Y$ atoms. For each composition the FM and FIM reference states were considered. In the case of FM state, all spins of Ni, Co, Mn$_Y$ and Mn$_Z$ atoms are parallel, while in the case of FIM state, the spin of Mn$_Z$ atom is reversed. The effect of chemical disorder is taken by using the single-site coherent-potential approximation (CPA). The Heisenberg exchange coupling constants were calculated, using the equation proposed by Liechtenstein et al. [13]. The maximum number of CPA iterations and the CPA tolerance were set to 20 and 0.01 mRy, respectively. The first step in these calculations is to calculate the self-consistent potential (SCF). For SCF cycles, the scattering path operator was calculated with the special point method using a regular k-mesh grid of 57$^3$ with 4495 k points. All calculations were converged to 0.01 mRy of the total energy.

To achieve this convergence, we have used the BROYDEN2 scheme [14] with the exchange-correlation potential of PBE. For the SCF calculations the arc-like contour path in the complex energy plane has been chosen as in approach of weakly bound states which are treated as core states. The upper end of the energy path $E_{\text{max}}$ is set to the Fermi energy $E_F$. Regarding the real part of lowest energy value we have used the value of $E_{\text{min}}^0 = -0.1$ Ry. The number of $E$-mesh points was set to 30. In order to achieve faster convergence, the SCF mixing parameter was set to 0.20. The maximum number of SCF iterations was taken to 200. The self-consistent potential, which was calculated for the optimized lattice parameter, is then used to calculate the exchange parameters and DOS. For that we have taken the spin-polarized scalar-relativistic (SP-SREL) Hamiltonian with an orbital momentum cutoff of $l_{\text{max}} = 2$ on a grid of 57$^3$, i.e., 4495 $k$ points. The exchange coupling parameters are calculated with respect to the central site $i$ of a cluster atoms with the radius $R_{\text{clu}} = \max [R_i - R_j]$. We have taken the radius of a sphere $R_{\text{clu}}$ of 2.0.

For the lattice parameters and $c/a$ ratio we have used the values listed in Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>$a_0$ (Å)</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{45}$Co$<em>5$Mn$</em>{37}$In$</em>{13}$</td>
<td>5.96</td>
<td>1.21</td>
</tr>
<tr>
<td>Substitution of C for In</td>
<td>5.845</td>
<td>1.33</td>
</tr>
<tr>
<td>Substitution of C for Mn</td>
<td>5.85</td>
<td>1.35</td>
</tr>
</tbody>
</table>

2.1 Magnetic exchange parameters

In this subsection we present results of ab initio calculations of magnetic exchange coupling constants of carbon-doped Ni-Co-Mn-In alloys. The Heisenberg exchange parameters were calculated with the SPR-KKR package and lattice parameter $a_0$ and fixed $c/a$ ratio. Note that the lattice parameters for martensite were taken from the condition considering that a cell volume does not change with tetragonal distortions.

Figures 1 and 2 show the calculated $J_{ij}$ exchange parameters in austenite and martensite of C-doped Ni-Co-Mn-In alloys calculated for different spin configurations. Here, we consider two compositions with the substitution of 5% C for In and for Mn$_Y$ atoms. In order to compare results, we also present here the exchange interactions for the case of Ni$_{45}$Co$_5$Mn$_{37}$In$_{13}$ alloy.

With respect to the $J_{ij}$ interactions of austenite in Fig. 1, we see that the carbon addition increases both, the FM Mn$_Y$(Z)-Co interaction and the AFM Mn$_Y$-Mn$_Z$ interaction between nearest neighbors atoms as well as Mn-Ni interaction does not practically change. Large Mn-Co and Mn-Ni interactions in the first coordination shell are responsible for a high Curie temperature of austenite. Note that these large interactions also due to the short distance between Mn and Co, Ni atoms (in a case that Co substitutes for Ni).
Regarding the exchange parameters of martensite in C-doped Ni-Co-Mn-In alloys shown in Fig. 2, it is seen that the AFM Mn Y-MnZ interaction increases while the FM Mn-Co and Mn-Ni interactions decreases with carbon addition. Besides, the Mn Y-MnZ interaction shows the most striking oscillatory behavior from AFM to FM interaction. As the result, this interaction in the first coordination shell has a large AFM value of $J_{ij}/g \approx 15 \text{ meV}$ and then it changes sign and reaches large FM value in the next coordination shell. The enhancement of AFM interaction between Mn atoms in martensite can be related with decrease in the lattice parameters $a$ and $b$ leading to a reduction in the Mn Y-MnZ distance. Generally, low values of the Curie temperature of martensite are expected because of weak FM interactions between Mn and Co, Ni atoms and strong AFM interactions between Mn atoms.

### 2.2 Density of states

The calculated spin-polarized total and partial DOS of FM austenite and of FIM martensite in C-doped Ni-Co-Mn-In alloys are presented in Fig. 3 and 4, respectively. First, let us discuss the DOS curves in FM austenite.

It can be seen from Fig. 3 that the antibonding parts of the DOS around and above the Fermi level $E_F$ have mostly contributions from Mn Y and MnZ $3d$ states, while bonding parts and non-bonding parts have Mn Y, MnZ, and Ni $3d$ contributions. Besides, the small peak at -10 eV on the total DOS is related with the contribution of the $s$ electronic states of carbon. In general, for spin-up electronic states two main peaks below the $E_F$ in the Mn Y and MnZ $3d$ states coincide with peaks of the Ni $3d$ states, resulting the strong coupling between atoms.

Regarding the DOS curves for martensite of C-doped Ni-Mn-In alloys, we can see from Fig. 4 that it consists also of the lower part containing mainly $s$-states of carbon at -10 eV and the higher bonding and antibonding parts. The antibonding parts of the DOS around and above the $E_F$ have dominantly $3d$-states of Mn Y, MnZ atoms, while bonding parts have Mn Y and Ni $3d$ contributions. The difference of contributions to bonding and non-bonding parts for austenite and martensite is associated with the reversed magnetic moment of Mn Z in martensite compared to their parallel magnetic moment in
Additionally, for spin-up anti-bonding states the small peak observed above $E_F$ is caused by contributions from Mn$_{Y}$ 3d bands. It is also found that the contributions from Mn$_{Y}$ and Mn$_{Z}$ 3d bands to the total DOS are opposite to each other. For the majority DOS of Mn$_{Y}$, the main two peaks below $E_F$ are occupied while for the minority DOS, the antibonding peak is above $E_F$. As the result, the total magnetic moment is found to reduce. We can also observe for austenite and martensite of the Ni$_{45}$Co$_5$Mn$_{37}$In$_8$C$_5$ alloy with substitution of 5% of C for Mn$_{Y}$ (Figs. 3(b) and 4(b)), that the partial DOS curves for both Mn$_{Y}$ and Mn$_{Z}$ atoms are similar because of close concentrations of Mn$_{Y}$ and Mn$_{Z}$ atoms in this compound. With respect to the 3d bands of Ni for both, austenite and martensite (Figs. 3 and 4), majority and minority spin states are practically symmetrical, which results in the small magnetic moment of Ni. Since the concentration of C and Co atoms is small, they contribute little to the total DOS. Finally, the pseudogap at the Fermi level is found from Fig. 4 providing the stabilization of the martensitic phase.

![Figure 4. Total and partial DOS curves for FIM martensite of (a, b) C-doped Ni$_{45}$Co$_5$Mn$_{37}$In$_{13}$ and (c) Ni$_{45}$Co$_5$Mn$_{37}$In$_{13}$ alloys.](image)

### 3 Monte Carlo details and results

#### 3.1. $q$-state Potts Hamiltonian

The magnetic exchange parameters in a combination with partial magnetic moments can be used to simulate a temperature behavior of magnetization and determine $T_{C}^{d}$ and $T_{C}^{M}$ temperatures by means of MC method. In MC simulations, we use the real lattice with periodic boundary conditions. The unit cell of Heusler alloys is comprised of four interpenetrating fcc sublattices with In at site $(0, 0, 0)$, Mn at $(1/2, 1/2, 1/2)$ and Ni at sites $(1/4, 1/4, 1/4)$ and $(3/4, 3/4, 3/4)$, respectively. For the construction of C-doped Ni$_{45}$Co$_5$Mn$_{37}$In$_{13}$ alloys, the configurations of Co, Mn$_{Y}$ and C atoms on the Ni, In, and Mn$_{Y}$ sublattices, respectively, take randomly and their total number are fixed by nominal composition.

In this study we use the $q$-state Potts Hamiltonian, which allows us to simulate the first and second order magnetic phase transitions [15]. Here, $q$ is the number of possible spin states, $2S + 1$. Since magnetic moments of C and In atoms are negligible, we consider only three types of magnetic atoms in C-doped Ni-Co-Mn-In. As the result, we use the mixed 3-4-6 Potts model. Where, 3, 4, and 6 correspond to the maximum possible spin states for Ni, Co, and Mn$_{Y}$ [14]. The magnetic Hamiltonian without external magnetic field may be written as

$$H_{\text{mag}} = -\sum_{\langle i,j \rangle} J_{ij} \delta_{S_i, S_j}.$$  

Here, $J_{ij}$ are the exchange parameters obtained from $ab$ initio calculations, which may become FM ($J_{ij} > 0$) or AFM ($J_{ij} < 0$). $S_i$ is a spin defined on the lattice site $i = 1...N$. The Kronecker symbol, $\delta_{S_i, S_j}$, restricts spin-spin interactions to the interactions between the same $q$(Mn$_{Y/Z}$), $q$(Co), and $q$(Ni) states. The summation is taken over neighbor pairs up to the six coordination shells.

The magnetization of the 3-4-6 state Potts model is defined in the following way:

$$m_n = \frac{1}{N_n} \left( q_n N_n^{\text{max}} - N_n \right),$$  

where, $n$ denotes a magnetic atom type (Ni, Co, Mn$_{Y}$, or Mn$_{Z}$), $N_n$ is the total number of type of atom $n$, $q_n$ is the number of magnetic states of atom type $n$, and $N_n^{\text{max}}$ is the maximum number of identical magnetic states on the lattice of type of atom $n$. The total magnetization C-doped Ni$_{45}$Co$_5$Mn$_{37}$In$_{13}$ alloys can be written as

$$M = \mu_0 m_n (1-x) + \mu_0 m_{n_n} x + \mu_{n_n} m_{n_{n_n}} + \mu_{n_{n_n}} m_{n_{n_{n_n}}},$$  

where, $x$ and $y$ are the concentrations of Co and Mn$_{Z}$ atoms, respectively. $\mu_n$ are the magnetic moments of Ni, Co, Mn$_{Y}$, and Mn$_{Z}$ atoms calculated from $ab$ initio simulations and listed in Table 2.
3.2 Model results

In this section we present results of modelling a temperature behavior of magnetization curves for austenite and martensite of C-doped Ni₄₅Co₅Mn₃₇In₁₃ alloys. The MC calculations carried out by means of the classical Metropolis algorithm. Change in the independent variables \( q(Ni), q(Co) \) and \( q(MnYZ) \) are accepted or rejected according to a single-site transition probability \( W = \{ 1, \exp(-\Delta H_{mag}/k_BT) \} \), where \( k_B \) is the Boltzmann constant. The number of sites used in the simulation is 3925. Thus, in the stoichiometric case, Ni₃Mn₁₈, we have a lattice containing 1098 MnY, 1728 Ni, and 1099 In atoms. As noted above, for off-stoichiometric compositions, the random distribution of MnY, Co, and C atoms at the In, Ni, and MnY sublattices was proposed. As time unit, we used one MC step consisting of \( N \) attempts to change the \( q \) variables. For a given temperature, the number of MC steps at each site was \( 5 \times 10^3 \). The simulations started from the FM austenite and FIM martensite. The system energy \( H_{mag} \) and the order parameter \( m \) (magnetization) were averaged over 1225 configurations for each of the 400 MC steps. In order to obtain equilibrium values of \( H_{mag} \) and \( m \), the first \( 10^4 \) MC steps were discarded. The magnitudes of spin states (i.e. \( q \) variables) were taken to correspond to a random number \( r \), \( 0 \leq r \leq 1 \), according to the scheme: if \( 0 \leq r \leq 1/3 \), consequently \( q(Ni) = l \), \( l = 1, 2, 3 \), if \( 0 \leq r \leq k/4 \), consequently \( q(Co) = k \), \( k = 1 \ldots 4 \), finally, if \( 0 \leq r \leq l/6 \), consequently \( q(MnYZ) = t \), \( t = 1 \ldots 6 \).

The temperature behaviors of magnetization curves for austenite and martensite of C-doped Ni₄₅Co₅Mn₃₇In₁₃ alloys are shown in Fig. 5. We can see that the addition of carbon results in decrease in the Curie temperatures of austenite and martensite as compared with the Ni₄₅Co₅Mn₃₇In₁₃ alloy. In the cases of compounds with substitution of C for In and MnY atoms, we can see that the \( T_{C,M} \) temperatures are similar \( (T_{C,M} \approx 210 \text{ K}) \), whereas the \( T_{C,A} \) temperatures are slightly different. For instance, the compound with substitution 5 \%at. of C for MnY have \( T_{C,A} \) about of 350 K while for other alloy, it is closed to 320 K. In general, the decrease in Curie temperatures with carbon addition is related to enhancement of AFM interactions between Mn and to reduction of FM Mn-Ni and Mn-Co interactions.

4 Conclusions

In this study, we combined the \textit{ab initio} and Monte Carlo calculations to investigate the magnetic and electronic properties of carbon-doped Ni₄₅Co₅Mn₃₇In₁₃ Heusler alloys. Two magnetic spin configurations referred as FM and FIM were considered. It was shown that the addition of carbon resulted to an increase in the FM MnY-Z-Co interaction and the AFM MnY-MnZ interactions between nearest neighbors atoms in austenite. Contrary to that in the case of martensite, it was found an enhancement of AFM interactions between Mn and a reduction of FM Mn-Ni and Mn-Co interactions with carbon doping. As the result, a decrease in the Curie temperatures of austenite and martensite has been observed. However, the large change in a magnetization between austenite and martensite was observed. Therefore, we can assume that carbon-doped Ni-Co-Mn-In Heusler alloys are interesting materials in the field of magnetic cooling technology. The modelling of MCE in such compounds still needs to be considered, but this is beyond the scope of this study.

Acknowledgments

This work is supported by RFBR Grant No. 14-02-01085, RSF No. 14-12-00570/14 (Section 2), Ministry of Education and Science of Russian Federation (RF) No 3.2021.2014/K (Section 3). PE acknowledges DFG (SPP 1599) for financial support.

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