ФИЗИКА

Chelyabinsk Physical and Mathematical Journal. 2016. Vol. 1, iss. 2. P. 117–123.

УДК 538.9

REFERENCE STATES OF Cr-DOPED Ni-Co-Mn-(In, Sn) ALLOYS: INSIGHTS FROM FIRST PRINCIPLES STUDY

V.D. Buchelnikov[1,a], **V.V. Sokolovskiy**[1,2,b], **M.A. Zagrebin**[1,c]

[1] *Chelyabinsk State University, Chelyabinsk, Russia*
[2] *National University of Science and Technology "MIS&S", Moscow, Russia*
[a] *buche@csu.ru;* [b] *vsokolovsky84@mail.ru;* [c] *miczag@mail.ru*

In this paper we report on the equilibrium magnetic and structural reference states of complex Cr-doped Ni-Co-Mn-(In, Sn) Heusler alloys, which are studied from first-principles within the density functional theory. The off-stoichiometric compositions were treated by using the supercell approach with different atomic distributions of excess Mn and In atoms. Supercells of 16 and 32 atoms were used. Three different ferrimagnetic and one ferromagnetic spin configurations were considered. The results of energy relaxation calculations have been averaged over different atomic distributions. It is found that for 16 atoms supercell the ferromagnetic (ferrimagnetic) state in austenite and a ferrimagnetic state in martensite are favorable for $Ni_7Co_1Mn_5Cr_1In(Sn)_2$, respectively. While for 32 atoms supercell of $Ni_{14}Co_2Mn_{11}Cr_1(In, Sn)_4$ the ferromagnetic (a ferrimagnetic) spin configuration in austenite (martensite) is energetically stable, respectively.

Keywords: *Heusler alloys, supercell approach, magnetic reference state, ab initio calculations.*

1. Introduction and preliminaries

As it is known, Co-doped Ni-Mn-Z (Z = Ga, In, Sn) Heusler alloys exhibit unique multifunctional properties such as the magnetic shape memory effect, magnetic-field-induced strains, exchange bias effect, giant magnetoresistance and the magnetocaloric effect (MCE), which are promising for future technologies [1–5]. The most of these effects are associated with the complex magnetic ordering below the austenite-martensite transformation [6–8]. As a result, the characteristic magnetization changes across the martensitic transformation are experimentally and theoretically observed due to the strong competition between ferromagnetic (FM) and antiferromagnetic (AFM) interactions [2; 5; 6; 8]. The main reason of large AFM correlations is associated with decrease in a distance between the nearest Mn_Y and Mn_Z atoms located at the Mn and Z sublattices. Recent studies found experimentally that Mn enriched samples and addition of Co may lead to quite pronounced values for the adiabatic temperature change across the martensitic transformation with $\Delta T_{ad} \approx -6$ and -8 K for $Ni_{45.2}Co_{5.1}Mn_{36.7}In_{13}$ and $Ni_{45.7}Co_{4.2}Mn_{36.6}In_{13.5}$ alloys upon variation of magnetic field from 0 to 1.95 T [2; 5], respectively, which are significantly higher than that reported for other Heusler alloys and are due to the highly dominant structural contribution in these systems.

This work is supported by RFBR Grant No. 14-02-01085, Russian Science Foundation (RSF) No. 14-12-00570 (Section 3), Ministry of Education and Science of Russian Federation (RF) No. 3.2021.2014/K (Section 2), President RF Grant MK-8480.2016.2.

In our previous works [9; 10], in order to solve the problem of MCE optimization in the $Ni_{1.75}Co_{0.25}Mn_{1.5}In_{0.5}$ alloy we investigated theoretically the influence of Cr addition on its magnetic and magnetocaloric properties using both first-principles and Monte Carlo calculations. As a result, the large inverse MCE was observed in the vicinity of magnetostructural transformation from the ferrimagnetic (FIM) martensite to the FM austenite upon heating suggesting that magnetic moments of Cr and Mn_Z change their orientation during the transformation. This result was obtained by using one set of atomic distribution in the 16-atoms supercell. The aim of this work is an additional *ab initio* study of various atomic distributions in supercells of 16 and 32 atoms on the equilibrium reference states of complex Cr doped Ni-Co-Mn-(In, Sn) Heusler alloys.

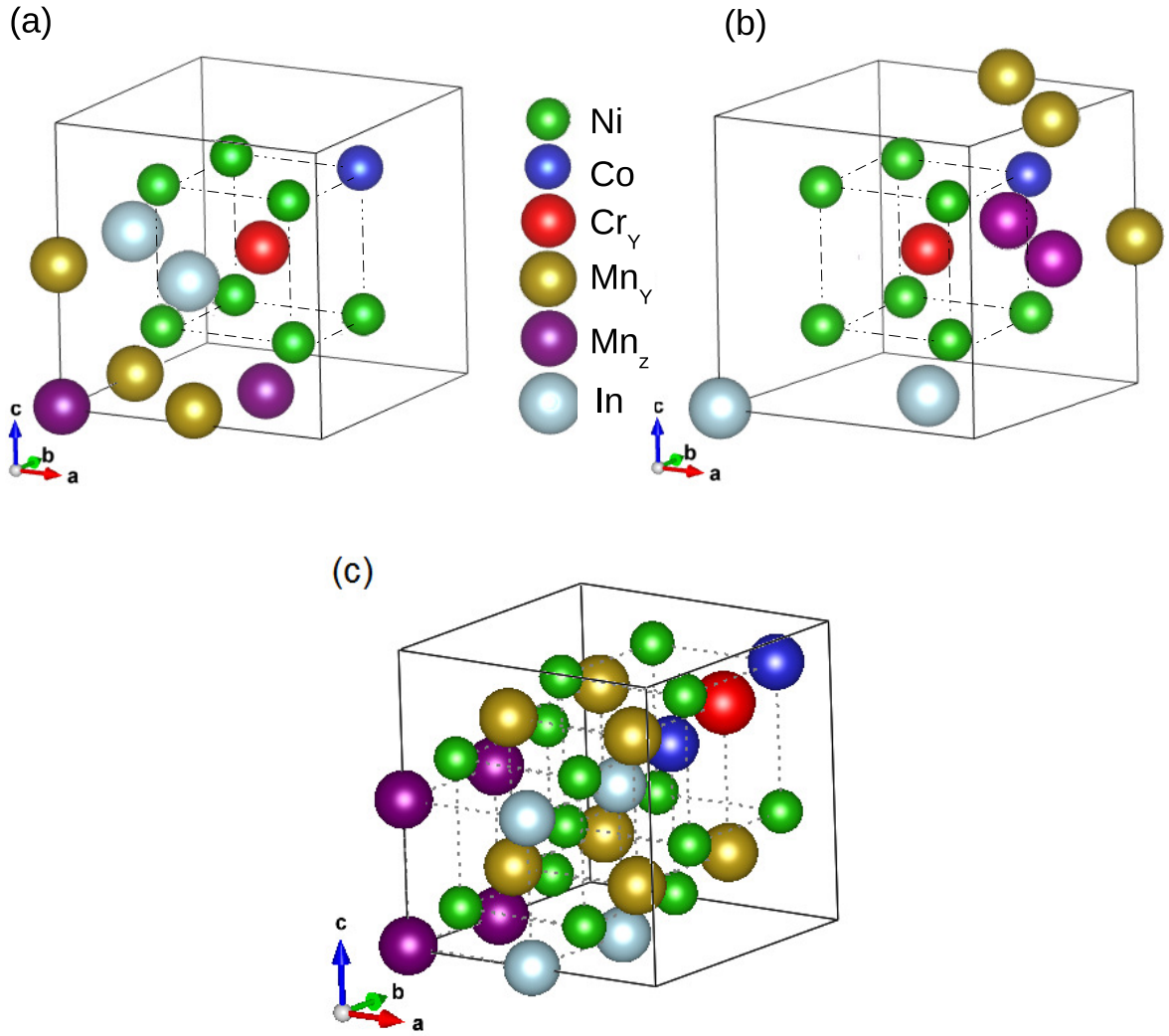

Fig. 1 (Colour online). (a, b) Two types of 16-atom and (c) 32 atoms supercells for off-stoichiometric $Ni_7Co_1Mn_5Cr_1(In, Sn_2)$ and $Ni_{14}Co_2Mn_{11}Cr_1(In, Sn)_4$ Heusler alloy were used

2. Computational details

The calculations have been performed using the *ab-initio* total-energy and molecular dynamics program VASP (Vienna *ab-initio* simulation program) developed at the Fakultät für Physik of the Universität Wien [11; 12]. The interaction between ions and electrons was described by the projector-augmented wave (PAW) method [12; 13]. PAW pseudopotentials in the VASP code allow for a considerable reduction in the number of plane-waves per atom for transition metals. The generalized gradient approximation (GGA) in Perdew and Wang parameterization [14] was used to describe

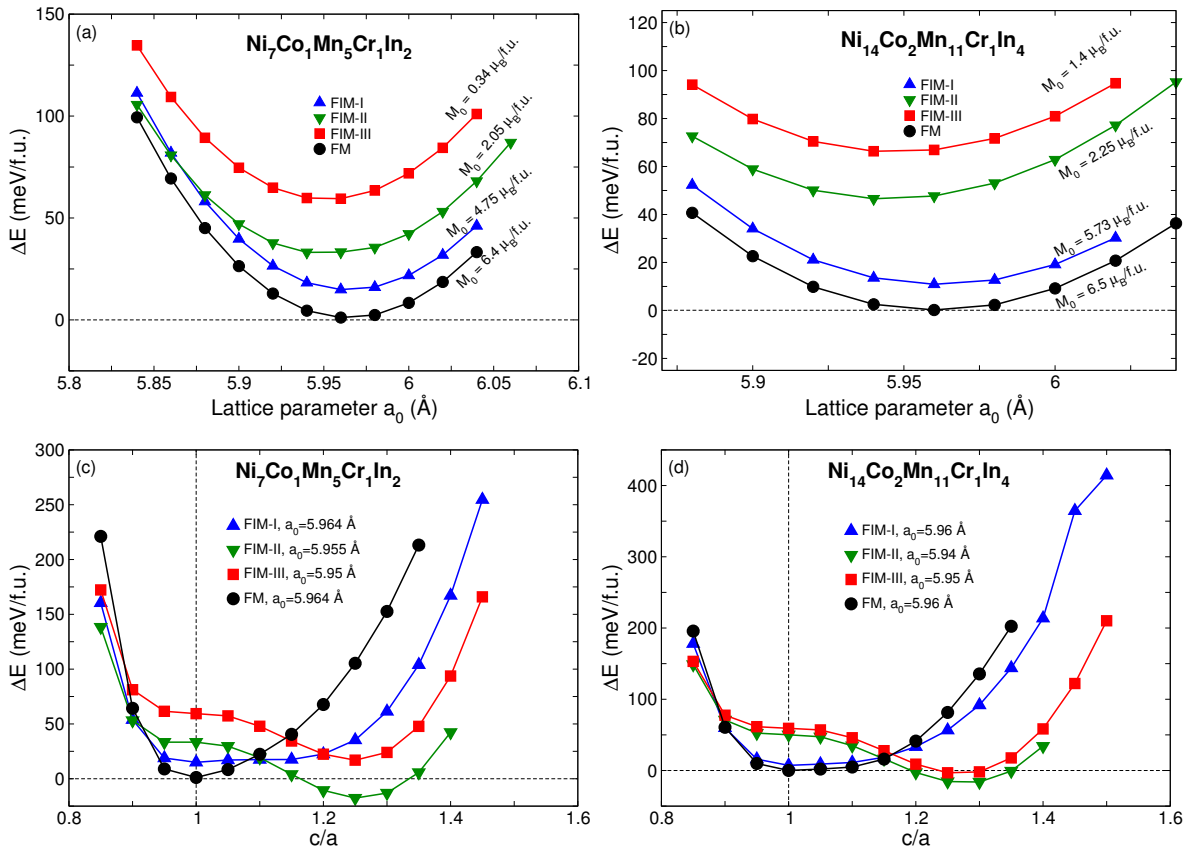

Fig. 2. The variation of the total energy as a function of (a, b) lattice parameter and (c, d) tetragonality c/a for 16 and 32 atoms supercells of $Ni_7Co_1Mn_5Cr_1In_2$ and $Ni_{14}Co_2Mn_{11}Cr_1In_4$ with different magnetic configurations, respectively. Here, all results were averaged over different atomic distributions and distortions (tetragonal (along z axis) and orthorhombic (along x, y axes))

the exchange-correlation energy and up to now it is the best approach to describe the magnetic materials. For the pseudopotentials used, the electronic configurations are $Ni(3p^63d^84s^2)$, $Co(3d^84s^1)$, $Mn(3p^63d^54s^2)$, $Cr(3p^63d^54s^1)$, $In(4d^{10}5p^15s^2)$, and $Sn(4d^{10}5p^25s^2)$, respectively. The kinetic energy cut-off was 400 eV and the kinetic energy cut-off for the augmentation charges was 800 eV. A Monkhorst — Pack grid [15] was employed to sample the Brillouin zone. The **k**-points in the Brillouin zone for self-consistent field cycles were generated with 8^3 and 12^3 meshes for c/a and lattice relaxation calculations. The performed calculations were semirelativistic and the spin polarization was taken into account for all the cases. All considered structures were relaxed using the conjugate gradient algorithm and both the atomic position and the volume were optimized. In order to calculate the tetragonal distortions of the cubic structure, we were fixed the volume of a supercell as $V_0 = a_0^3 \approx a^2c$.

In the *ab initio* calculations, we treated off-stoichiometric compositions of Ni-Co-Mn-Cr-(In, Sn) using the supercell approach. Supercells of 16 and 32 atoms corresponding to the austenite structure are shown in Fig. 1. Here, we consider that Co (Cr) substitutes here for Ni (Mn_Y) because of the atomic radius of Co and Ni (Mn and Cr) atoms is approximately the same, respectively. In order to show another atomic configuration, we present two types of 16 atoms supercell. We used next cells: $Ni_7Co_1Mn_5Cr_1(In, Sn)_2$ (16 atoms) and $Ni_{14}Co_2Mn_{11}Cr_1(In, Sn)_4$ (32 atoms) which correspond to the chemically disordered compositions $Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}(In, Sn)_{0.5}$ and $Ni_{1.75}Co_{0.25}Mn_{1.375}Cr_{0.125}(In, Sn)_{0.5}$. Such cells were chosen because of they are close to the composition $Ni_{1.8}Co_{0.2}Mn_{1.48}In_{0.52}$ without Cr which exhibits the large ΔT_{ad} [2; 5]. As a result, the composition can be varied by 6.25 at.% and 3.125 at.% when replacing

one atom by another type of atom, respectively.

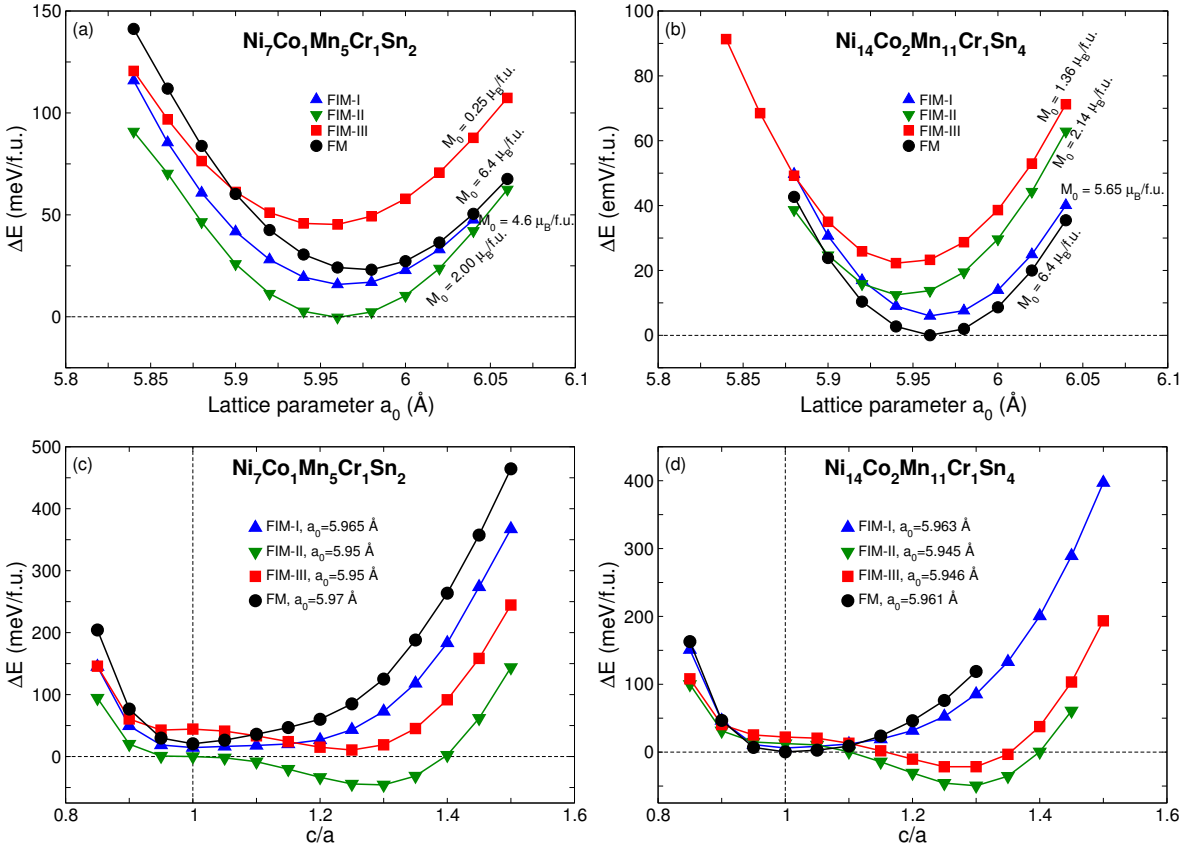

Fig. 3. The variation of the total energy as a function of (a, b) lattice parameter and (c, d) tetragonality c/a for 16 and 32 atoms supercells of $Ni_7Co_1Mn_5Cr_1Sn_2$ and $Ni_{14}Co_2Mn_{11}Cr_1Sn_4$ with different magnetic configurations, respectively. Here, all results were averaged over different atomic distributions and distortions (tetragonal (along z axis) and orthorhombic (along x, y axes))

Besides, *ab initio* calculations have been carried out for four magnetic configurations referred to as the FM state (all magnetic moments of Ni, Co, Cr, Mn_Y, and Mn_Z are parallel) and three FIM states: FIM-I (spin of Cr on either X, Y or Z lattice is reversed), FIM-II (spins of Mn_Z are reversed), and FIM-III (spins of Mn_Z and Cr are reversed).

3. Results of *ab initio* calculations

In order to find the optimized lattice parameters of Ni-Co-Mn-Cr-(In, Sn) in the $L2_1$ structure, we calculated the changes in the total energy as a function of lattice parameter. Energy curves were computed for different magnetic reference states (FM and FIM ones) using the 16 and 32 atoms supercells. Further, we did the total energy calculations for tetragonal distortions with the set of optimized lattice constants in Ni-Co-Mn-Cr-(In, Sn) alloys. The results of these investigations are shown in Fig. 2 and Fig. 3.

In Figs. 2 (a, b) we present the results of lattice relaxation for Ni-Co-Mn-Cr-In alloys. It can be seen from the figures that for both 16 and 32 atoms supercells, the FM spin configuration in austenite is energetically favorable compared to FIM configurations. Therefore, a maximum total magnetic moment ($\mu_{tot} \approx 6.5\ \mu_B$/f.u.) for austenite is found. It should be noted that the calculated lattice parameter of FM $Ni_7Co_1Mn_5Cr_1In_2$ in austenite (5.964 Å) is in a good agreement with experimental value ($a_0 = 5.96$ Å) for $Ni_{45}Co_5Mn_{37}In_{13}$ [2; 5] and theoretical value (5.98 Å) for $Ni_7Co_1Mn_5Cr_1In_2$ [9; 10]

obtained by using the Quantum Espresso (QE) package [16]. Besides, our results show that the lattice constant is not practically changed with increasing number of atoms in a supercell.

The variation of the total energy as a function of tetragonal distortion c/a of $Ni_7Co_1Mn_5Cr_1In_2$ and different magnetic ground states calculated for 16 and 32 atoms supercells, are shown in Figs. 2 (c, d). Evidently, upon tetragonal distortion the FIM-II spin configuration is stabilized with respect to the FM state which favors in austenite. However, in the case of 32 atoms supercell of $Ni_{14}Co_2Mn_{11}Cr_1In_4$, the FIM-II and FIM-III solutions are very close in energy.

It is important to emphasise that in this work we show averaged energy curves, $E(a)$ and $E(c/a)$, for Ni-Co-Mn-Cr-(In, Sn) compounds. Thus, all solutions have been averaged over different atomic distributions and distortions, namely, tetragonal (along z axis) and orthorhombic (along x, y axes) distortions. Previously, we have done similar calculations for $Ni_7Co_1Mn_5Cr_1In_2$ alloy without any averaging [9; 10]. Those calculations have been done using the QE code. Our results have shown that in the case of the first (second) 16-atoms supercell (See Figs. 1 (a, b)), the FM (FIM-I) spin configuration in austenite is stable, while the FIM-III (FIM-I) state in martensite is found to be favor, respectively. Therefore, we can suppose that if atomic distribution in a cell will be realized as shown in Fig. 1 (a) or a smaller amount of Cr element will be taken into account that the stable FIM-III martensite may appear.

The variations of the total energy of the 16 and 32 atoms supercells for Ni-Co-Mn-Cr-Sn system as a function of the lattice parameter for different spin configurations are presented in Figs. 3 (a, b). These results show that the stable FIM-II spin configuration in austenite changes by the FM one with decreasing Cr content. As a result, the total magnetic moment for austenite is found to increase from $\mu_{tot} \approx 2.0$ to 6.4 μ_B/f.u. We also can observe that the optimized lattice constants for $Ni_7Co_1Mn_5Cr_1Sn_2$ and $Ni_{14}Co_2Mn_{11}Cr_1Sn_4$ compositions are closed to ones for Ni-Co-Mn-Cr-In systems.

In Figs. 3 (c, d) we present the results of c/a calculations for tetragonal distortion of the 16 and 32 atoms supercells for Ni-Co-Mn-Cr-Sn system. We have found that in the case of $Ni_7Co_1Mn_5Cr_1Sn_2$ composition, the structural transformation occurs without a magnetic phase transition. Since, the equilibrium magnetic configurations for both austenite and martensite are FIM-II, where only Mn_Z atoms have a negative magnetic moment. According to the $Ni_{14}Co_2Mn_{11}Cr_1Sn_4$ composition with a smaller Cr content, the austenite-martensite transformation can be accompanied by the magnetic transition from FM austenite to FIM-II or FIM-III martensite. The small difference between FIM-II and FIM-III solutions can be seen from Fig. 3 (d). The same trend is observed for Ni-Co-Mn-Cr-In system with a smaller Cr content. As a result, the large changes in magnetizations across the magnetostructural phase transition for both $Ni_{14}Co_2Mn_{11}Cr_1(In, Sn)_4$ compositions are expected.

4. Conclusion

In conclusion, we have performed *ab initio* calculations of the total energy change as a function of lattice parameter and tetragonal ratio (c/a) in Ni-Co-Mn-Cr-(In, Sn) Heusler alloys. From these calculations, the equilibrium total energies, magnetic moments, and relaxed structures at ground state have been calculated on the 16 and 32 atoms supercells with different atomic distributions. Four types of magnetic states labelled as FM, FIM-I, FIM-II, and FIM-III have been used. The results of energy calculations have been averaged over different atomic distributions and tetragonal/orthorhombic distortions. The magnetostructural phase transition from FM

austenite to FIM-II martensite have been clearly observed for $Ni_7Co_1Mn_5Cr_1In_2$, $Ni_{14}Co_2Mn_{11}Cr_1In_4$, and $Ni_{14}Co_2Mn_{11}Cr_1Sn_4$. While in the case of $Ni_7Co_1Mn_5Cr_1Sn_2$, the martensitic transformation occurs without any magnetic transition. We have found that for Ni-Co-Mn-Cr-(In, Sn) compositions with a smaller amount of Cr (3.125 at.%), the both FIM-II and FIM-III solutions have a pronounced minimum of the energy. Moreover, the FIM-II and FIM-III solutions in martensite are very close in energy. In this connection we can suggest that the martensitic phase have a complex magnetic structure where FIM-II and FIM-III spin configurations may coexist. As a consequence of different magnetic reference states in austenite and martensite, the large changes in magnetization across the magnetostructural phase transition are expected for Ni-Co-Mn-Cr-(In, Sn) systems. This shows again how subtle the magnetization reacts to environmental effect such as a disorder, defects, spin configurations etc. Calculations for larger supercells and more different spin configurations would be needed in order to perform a statistical averaging regarding the effects of atomic disorder and different spin configurations on the magnetization behavior.

References

1. **Das R., Sarma S., Perumal A., Srinivasan A.** Effect of Co and Cu substitution on the magnetic entropy change in $Ni_{46}Mn_{43}Sn_{11}$ alloy. *Journal of Applied Physics*, 2011, vol. 109, 07A901-4.
2. **Liu J. et al.** Giant magnetocaloric effect driven by structural transitions. *Nature Materials*, 2012, vol. 11, pp. 620–626.
3. **Cong D.Y., Roth S., Schultz L.** Magnetic properties and structural transformations in Ni-Co-Mn-Sn multifunctional alloys. *Acta Materialia*, 2012, vol. 60, pp. 5335–5351.
4. **Fabbrici S. et al.** Co and In doped Ni-Mn-Ga Magnetic shape memory alloys: a thorough structural, magnetic and magnetocaloric study. *Entropy*, 2014, vol. 16, pp. 2204–2222.
5. **Gottschall T. et al.**, Large reversible magnetocaloric effect in Ni-Mn-In-Co. *Applied Physics Letters*, 2015, vol. 106, 021901-4.
6. **Sokolovskiy V.V., Zagrebin M.A., Buchelnikov V.D.** Novel achievements in the research field of multifunctional shape memory Ni-Mn-In and Ni-Mn-In-Z Heusler alloys. *Materials Science Foundations*, 2015, vol. 81–82, *Shape Memory Alloys: Properties, Technologies, Opportunities*, N. Resnina and V. Rubanik eds., pp. 38–76.
7. **Planes A., Mañosa L., Acet M.** Magnetocaloric effect and its relation to shape-memory properties in ferromagnetic Heusler alloys. *Journal of Physics: Condensed Matter*, 2009, vol. 30, 233201-29.
8. **Comtesse D. et al.** First-principles calculation of the instability leading to giant inverse magnetocaloric effects. *Physical Review B*, 2014, vol. 89, 184403-6.
9. **Buchelnikov V.D. et al.** Magnetic states of the $Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}In_{0.5}$ Heusler alloy. *IEEE Transactions on Magnetics*, 2015, vol. 51, DOI: 10.1109/TMAG.2015.2438953.
10. **Sokolovskiy V.V. et al.** Achieving large magnetocaloric effects in Co- and Cr-substituted Heusler alloys: Predictions from first-principles and Monte Carlo studies. *Physical Review B*, 2015, vol. 91, 220409(R)-5.
11. **Kresse G., Furthmuller J.** Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, 1996, vol. 54, 11169-18.
12. **Kresse G., Joubert D.** From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B*, 1999, vol. 59, 1758-18.
13. **Blöchl P.E.** Projector augmented-wave method. *Physical Review B*, 1994, vol. 50, 17953-27.
14. **Perdew J.P., Wang Y.** Accurate and simple analytic representation of the electron-gas correlation energy. *Physical Review B*, 1992, vol. 45, 13244-6.

15. **Monkhorst H.J., Pack J.D.** Special points for Brillouin-zone integrations. *Physical Review B*, 1976, vol. 13, 5188-5.
16. Quantum ESPRESSO package Version 5.02. Availablle at: http://www.pwscf.org, accessed 10.05.2015.

Article received 17.05.2016
Corrections received 25.05.2016

Челябинский физико-математический журнал. 2016. Т. 1, вып. 2. С. 117–123.

ОСНОВНЫЕ СОСТОЯНИЯ Cr-ДОПИРОВАННЫХ СПЛАВОВ Ni-Co-Mn-(In, Sn): ВЫВОДЫ ИЗ ПЕРВОПРИНЦИПНЫХ ИССЛЕДОВАНИЙ

В. Д. Бучельников[1,a], **В. В. Соколовский**[1,2,b], **М. А. Загребин**[1,c]

[1] *Челябинский государственный университет, Челябинск, Россия*
[2] *Национальный исследовательский технологический университет «МИСиС», Москва, Россия*
[a] *buche@csu.ru;* [b] *vsokolovsky84@mail.ru;* [c] *miczag@mail.ru*

В данной статье мы сообщаем о равновесных магнитных и структурных основных состояниях сложных Cr-допированных сплавов Гейслера Ni-Co-Mn-(In, Sn), которые изучаются из первых принципов в рамках теории функционала плотности. Нестехиометрические композиции были получены с помощью подхода суперячейки с различными расположениями избыточных атомов Mn. Были использованы суперячейки из 16 и 32 атомов. Рассмотрены три различные ферримагнитные и одна ферромагнитная конфигурации спинов. Результаты расчётов геометрической оптимизации усреднены по различным атомным расположениям. Установлено, что для суперячейки из 16 атомов выгодны ферромагнитная (ферримагнитная) спиновая конфигурация и ферримагнитная спиновая конфигурация в мартенсите для $Ni_7Co_1Mn_5Cr_1In(Sn)_2$, в то время как для суперячейки из 32 атомов $Ni_{14}Co_2Mn_{11}Cr_1(In, Sn)_4$ (In, Sn)$_4$ энергетически выгодной является ферромагнитная (ферримагнитная) спиновая конфигурация в аустените (мартенсите).

Ключевые слова: *сплавы Гейслера, подход суперячеек, магнитное основное состояние, первопринципные вычисления.*

Поступила в редакцию 17.05.2016
После переработки 25.05.2016

Сведения об авторах

Бучельников Василий Дмитриевич, доктор физико-математических наук, профессор, заведующий кафедрой физики конденсированного состояния, Челябинский государственный университет, Челябинск, Россия; e-mail: buche@csu.ru.

Соколовский Владимир Владимирович, кандидат физико-математических наук, доцент кафедры физики конденсированного состояния, Челябинский государственный университет, Челябинск, Россия; научный сотрудник, Национальный исследовательский технологический университет «МИСиС», Москва, Россия; e-mail: vsokolovsky84@mail.ru.

Загребин Михаил Александрович, кандидат физико-математических наук, доцент кафедры радиофизики и электроники, Челябинский государственный университет, Челябинск, Россия; e-mail: miczag@mail.ru.