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First principles study of the structural properties of $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ Heusler alloy

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Abstract. In this work, the structural and magnetic properties of Cr – doped $Ni_{1.75}Co_{0.25}MnCr_{0.}5In0.5$ Heusler alloys are investigated by using the density functional theory calculations. The chemical disorder is treated by the 16-atom supercell approach. Three compositions with substitution of 6.25%, 12.5 %, 18.75%, and 25% Cr for Mn are taken into consideration. The formation energy, magnetic moments and lattice parameters depending on the Cr content are found. It is shown that compositions with 6.25% and 12.5% of Cr are energetically stable in austenite.

1 Introduction

Co -doped Heusler alloys Ni-Mn-Z (Z= Ga, In, Sn) have attracted a lot of attention due to the observation of shape memory effect, the giant magnetoresistance, magnetocaloric effect (MCE) etc. [1-4]. Thus, the Co addition can greatly change both the martensitic transformation temperature and Curie temperatures of austenite and martensite as well as it can change magnetization curves across the structural transition resulting in an enhancement of the inverse MCE. For instance, Liu et al. [5] directly measured the adiabatic temperature change (ΔT_{ad}) across the magnetostructural transformation for $Ni_{1.8}Co_{0.2}Mn_{1.48}In_{0.52}$ alloy upon variation of magnetic field from 0 to 1.9 T. The authors have found the largest value of ΔT_{ad} (≈ - 6 K) obtained for Heusler alloys.

Much less information is available about the Cr – doped influence on magnetic and magnetocaloric properties of Ni-Mn-In alloys. Sharma et. al. have concluded that the substitution of 2% Cr for Mn in a $Ni_{50}Mn_{34}In_{16}$ alloy leads to increase of an isothermal magnetic entropy change [6]. The influence of higher Cr content on MCE in $Ni_{50}Mn_{33-x}In_{17}Cr_x$ ($0 \leq x \leq 4$) has been studied by Sánchez-Alarcos et al. [7]. The authors have declared that the addition of high amount of Cr may be highly detrimental to the achievement of a large MCE.

In this work, we present theoretical investigations of the structural and magnetic properties as well as the relative stability of hypothetical $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ (x = 0.25, 0.50, 0.75, and 1.0) alloys in austenite.

2 Computational details

The equilibrium energy calculations were performed using the density functional theory as implemented in the Quantum ESPRESSO package [8]. The generalized gradient approximation for the exchange correlation functional in the formulation of Perdew, Burke and Ernzerhof (PBE) was used [9, 10]. The Kohn-Sham orbitals were described using a plane-wave basis set. An energy cutoff of 80 Ry was used to truncate the plane-wave expansion of the electronic wave functions. The Methfessel-Paxton smearing size was fixed at 5 mRy. In the calculations the automatically generated uniform grid of **k**-point as in Monkhorst-Pack grids was taken into account. The modeling parameters are calculated after an energy convergence of 0.01 mRy. A denser **k**-point mesh of 8^3 and the "smearing" occupation mode were used for calculations. It should be noted that in this work, we discuss calculation results for $Ni_7Co_1Mn_{6-x}Cr_xIn_2$ alloys (x = 1, 2, and 3) with ferromagnetic (FM) reference state in the framework of 16-atom supercell approach. This assumption is based on our recent energy calculations for Ni7Co1Mn6In2 composition [11]. Our *ab initio* calculations have shown that the FM spin configuration is energetically favorable as compared to other spin configurations. We would like also to point out that the parent theoretical composition, $Ni_7Co_1Mn_6In_2$ ($Ni_{1.75}Co_{0.25}Mn_{1.5}In_{0.5}$), is closed to experimental one, $Ni_{1.8}Co_{0.2}Mn_{1.48}In_{0.52}$, showing the largest inverse MCE [5].

In order to determine the phase stability of $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ alloys, we calculated the formation energy as difference between the total energy and partial total energies of the pure elements, as follows [11, 12]:

$$E_{form} = E_{tot}\left(Ni_7CoMn_{6-x}Cr_xIn_2\right) - \left(\frac{7}{16}\right)E_{Ni} - \left(\frac{1}{16}\right)E_{Co} - \left(\frac{6-x}{16}\right)E_{Mn} - \left(\frac{x}{16}\right)E_{Cr} - \left(\frac{2}{16}\right)E_{In}$$

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Here, $E_{tot}(Ni_7Co_1Mn_{6-x}Cr_xIn_2)$ is the total energy per formula cell and E_{Ni}, E_{Co}, E_{Mn}, E_{Cr}, and E_{In} are the total energy per atom of pure Ni, Co, Mn, Cr, and In unit cells, respectively.

3 Results of calculations

To determine the total energy of pure Mn element we considered both FM and antiferromagnetic (AF) alignments of magnetic moments in *bcc* and *fcc* structures. Our calculations have shown that the most energetically favorable configuration is the *fcc* structure with the FM spin configuration. In regard to the remaining elements, we used the *fcc*, simple hexagonal, and *bct* structures for Ni, Co, and In, respectively. Therefore, in the case of Co and In atoms we were carried out the structure relaxation calculations by two lattice parameters: *a* and *c*.

The total energy and equilibrium lattice parameters of pure Ni, Co, Mn, Cr, and In atoms are listed in Table 1. It should be noted that calculated lattice parameters are in a good agreement with the experimental data.

Table 1. Total energy and equilibrium lattice parameters of pure Ni, Co, Mn, Cr and In atoms.

Element	Total energy, Ry	lattice parameters, Å
Ni	-339.6066	a=3.528
Co	-74.417	a=2.51 c=4.07
Mn	-209.2766	a=3.49
Cr	-174.092	a=2.91
In	-136.6442	a=3.39 c=4.74

The variations of the total energy of the 16-atom supercells for $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ (x = 0.25, 0.5, 0.75, and 1.0) as a function of the lattice parameter are presented in Fig. 1. As can be seen from Fig. 1, the equilibrium lattice parameter of $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ alloys does not strongly change with the Cr addition. Besides, it is found to slightly decrease as compared with the parent $Ni_{1.75}Co_{0.25}Mn_{1.5}In_{0.5}$ compound [13].

The total energy of structure $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$, partial total energies of pure elements, and formation energy are listed in Table 2. We can see that in the case of x = 0.25 and 0.5, the total energy per atom of pure elements involved to $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ compositions is much higher than that total energy of the $Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}In_{0.5}$ and $Ni_{1.75}Co_{0.25}MnCr_{0.5}In_{0.5}$, suggesting that these compounds are stable in the austenite. In the latter cases, we can observe the opposite situation indicative of the not stable composition.

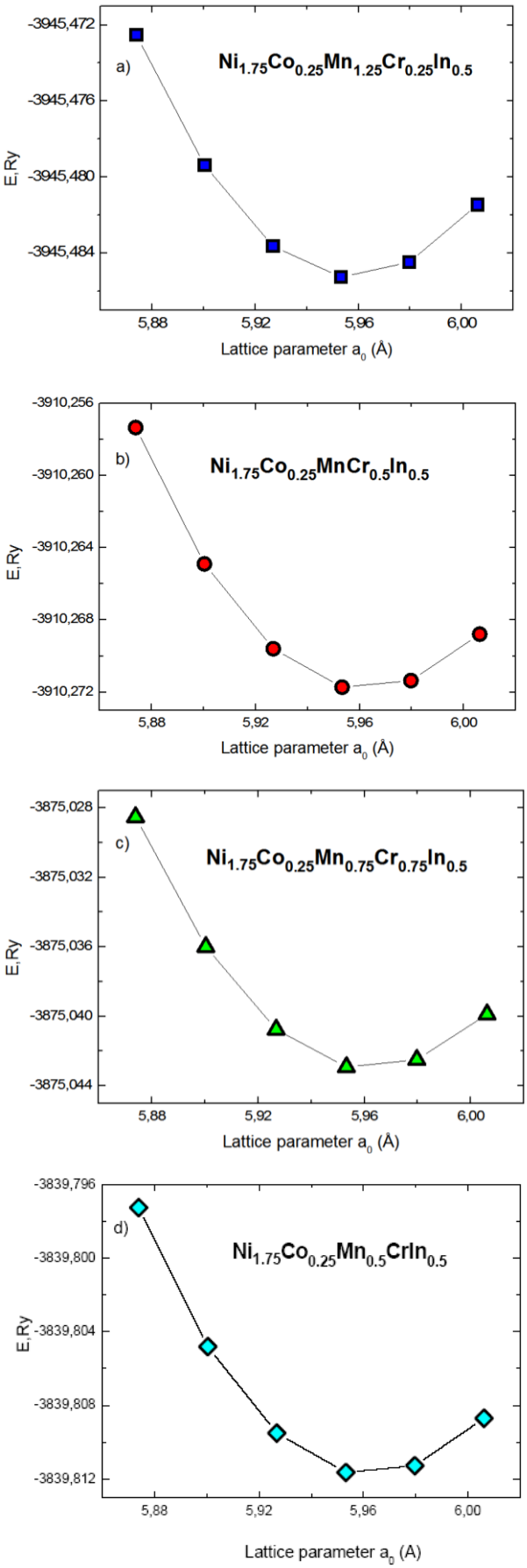

Figure 1. The variation of the total energy of the 16-atom supercells (a) $Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}In_{0.5}$, (b) $Ni_{1.75}Co_{0.25}MnCr_{0.5}In_{0.5}$, (c) $Ni_{1.75}Co_{0.25}Mn_{0.75}Cr_{0.75}In_{0.5}$, (d) $Ni_{1.75}Co_{0.25}Mn_{0.5}CrIn_{0.5}$ as a function of the lattice parameter.

Liu et al. has been observed the giant MCE effect in $Ni_{45}Co_5Mn_{37}In_{13}$ [5]. We were considered that the lattice parameter for $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ does not strongly change with Cr addition (Figure 1) and it was taken as a_0 = 5.96 Å for $Ni_{45}Co_5Mn_{37}In_{13}$ [5]. The total energy of structure $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ and partial total energies of the pure elements are listed in Table 2.

Table 2. The combinations of total energy for $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ alloys presented in (Ry).

Compositions	Total energy	Partial total energies
$Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}In_{0.5}$	-3945.4853	-3945.4266
$Ni_{1.75}Co_{0.25}MnCr_{0.5}In_{0.5}$	-3910.2717	-3910.242
$Ni_{1.75}Co_{0.25}Mn_{0.75}Cr_{0.75}In_{0.5}$	-3875.04303	-3875.0574
$Ni_{1.75}Co_{0.25}Mn_{0.5}CrIn_{0.5}$	-3839.8116	-3839.8728

Table 3. The formation energy for $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ alloys presented in (Ry).

Compositions	Formation energy
$Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}In_{0.5}$	-0.0587
$Ni_{1.75}Co_{0.25}MnCr_{0.5}In_{0.5}$	-0.0297
$Ni_{1.75}Co_{0.25}Mn_{0.75}Cr_{0.75}In_{0.5}$	0.0144
$Ni_{1.75}Co_{0.25}Mn_{0.5}CrIn_{0.5}$	0.0612

The equilibrium lattice parameters and magnetic moments depending on the Cr concentration are listed in Table 4. We found that the maximum total magnetic moment is observed for $Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}In_{0.5}$. Further increase of Cr content leads to decrease in the total magnetization.

Table 4. The lattice parameters and magnetic moments depending on the Cr concentration.

	Lattice parameters, Å	Magnetic moments, μ_B/f.u
$Ni_{1.75}Co_{0.25}Mn_{1.25}Cr_{0.25}In_{0.5}$	5.958	6.517
$Ni_{1.75}Co_{0.25}MnCr_{0.5}In_{0.5}$	5.963	6.285
$Ni_{1.75}Co_{0.25}Mn_{0.75}Cr_{0.75}In_{0.5}$	5.963	6.123
$Ni_{1.75}Co_{0.25}Mn_{0.5}CrIn_{0.5}$	5.962	5.964

4 Conclusion

In summary, the *ab initio* calculations have been carried out by using the 16-atom supercell approach. We have investigated the Cr-doped $Ni_{1.75}Co_{0.25}Mn_{1.5}In_{0.5}$ alloys with substitution of 6.25 %, 12.5 %, 18.75% and 25% Cr for Mn. In order to determine the phase stability of the $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ alloys, we calculated the formation energy as difference between the total energy of structure and partial energies for involved elements. It was shown that the total magnetic moment and energy of $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ alloys decrease with Cr content increasing. Besides, compositions with Cr content of 6.25 %, 12.5 % are found to stable in austenite in comparison to the composition with Cr content of 18.75% and 25%. The further additional calculations for the stability of $Ni_{1.75}Co_{0.25}Mn_{1.5-x}Cr_xIn_{0.5}$ alloys in martensite would be needed in order to understand the role of Cr in Ni-Co-Mn-In compounds.

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