

Effect of Co Substitution on Ni₂MnGe Heusler Alloy: *ab initio* Study

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Ab initio calculations shown that the Co substitution instead of Ni in Ni₂MnGe with the L₂₁ crystallographic structure leads to a decrease of the lattice constant and an increase of the total magnetic moment of the Ni_{2-x}Co_xMnGe compounds. The Mn(B) has the largest local moment above 3 μ_B coupled parallel to moments on the Ni(A,C) and Co(A,C), which are found in the ranges of 0.19 ÷ 0.26 μ_B for Ni(A,C) and 1.03 ÷ 0.97 μ_B for Co(A,C) for studied range of *x*. Using the results stemming from the total energy calculations, the values of bulk modulus and its pressure derivatives are estimated according to the Murnaghan EOS.

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1. Introduction

Heusler alloys have emerged as one of interesting topic in materials science, triggering a multitude of research activities with a focus on both fundamental science as well as tailored applications. Partial or complete substitution of atoms by various elements or changing of relative concentrations of atoms in well-known Heusler alloys can help in tuning of their various properties [1, 2]. The magnetic properties of Ni_{2-x}Co_xMnGe (0 ≤ *x* ≤ 1.0) system should be interesting because from first principles calculations the end compounds Ni₂MnGe and Co₂MnGe provide two different possibilities of application. The Co₂MnGe was predicted to be half metals if ferromagnetic states are assumed [3]. However, the other end compound Ni₂MnGe in the full ordered L₂₁ structure is a typical metal [4]. The properties of ferromagnetic ground state of Ni₂MnGe Heusler alloy as well as the magnetic properties under hydrostatic pressure have been reported in [4]. The studies of Ni or Fe substitution at B site in Ni₂MnGe in the framework of the coherent potential approximation or the virtual crystal approximation demonstrated that the total spin magnetic moment decreases with increase of Ni or Fe concentration [5, 6]. However, the magnetic properties of Ni₂MnGa_{1-x}Ge_x have remained basically unchanged due to substitution at D site [7].

The experimental evidence for Ni₂MnGe is that the site disorder can hardly be avoided completely in epitaxial Ni₂MnGe film grown by molecular beam epitaxy [8]. Perfect site order in the Heusler unit cell is difficult to achieve even in bulk single crystals. Thus, some of attempts to obtain samples with ordered structure are directed to substitution of one element by another atoms.

One of motivations for studying the Ni_{2-x}Co_xMnGe (0 ≤ *x* ≤ 2.0) is to search how A site substitution influ-

ences to electronic properties of the systems. The effect of Co-substitution on magnetic properties of Ni₂MnGe will be discussed at *ab initio* level using results of the FPLO-CPA calculations.

2. Computational tools

The numerical calculations were done using the full-potential nonorthogonal local orbital basis (FPLO) scheme [9, 10] within the local spin density approximation (LSDA). In the scalar-relativistic calculations the exchange and correlation potential of the Perdew and Wang was chosen [11]. The atomic disorder at the specific site was treated as the Coherent Phase Approximation (CPA), covered by the CPA solver described in [12]. The unit cell of the studied Ni_{2-x}Co_xMnGe (0 ≤ *x* ≤ 2.0) system is the cubic L₂₁, which contains four interpenetrating *fcc* sublattices at A(0 0 0), B($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$), C($\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$) and D($\frac{3}{4}$ $\frac{3}{4}$ $\frac{3}{4}$) sites. In the end compound Ni₂MnGe, these sites are occupied by Ni, Mn, Ni and Ge atoms, respectively. In present calculations, the A and C positions are occupied both by Ni and Co atoms. The following concentrations of Co atom are considered: *x* = 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8. The Brillouin zone (BZ) is sampled by *k*-mesh containing 256 points in its irreducible part. The other details of the FPLO calculation were similar to [5].

3. Results

We studied electronic structure of Ni_{2-x}Co_xMnGe assuming that Co atoms are simultaneously located at A and C site in the unit cell. The decrease in lattice constant of Ni₂MnGe with Co-substitution was obtained (Table I).

The total electronic densities of states (DOS) of the studied system (Fig. 1) show that the reconstruction of the spin dependent bands with Co substitution is mainly driven by hybridisation. The smearing of some peaks in the total DOS for spin-down direction with an increase

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of Co concentration is observed. The high peak of the DOS for spin-up direction in proximity of the Fermi energy (E_F) was obtained for $\text{Ni}_{1.8}\text{Co}_{0.2}\text{MnGe}$. However, for higher Co concentration ($x \geq 0.4$) this peak is shifted below the Fermi level. The partial filling of some valleys between main peaks in the total DOS for spin-up direction are visible with an increase of Co concentration.

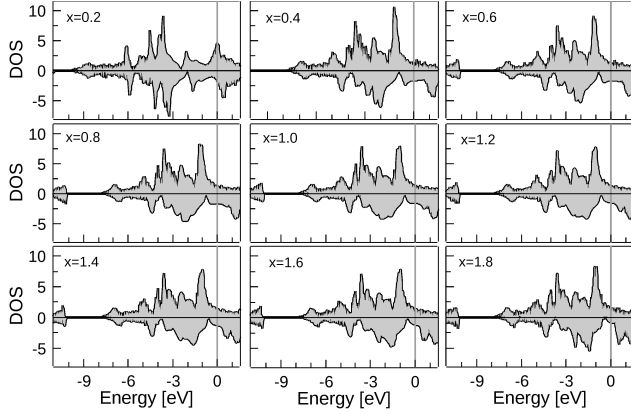


Fig. 1. Total density of states of $\text{Ni}_{2-x}\text{Co}_x\text{MnGe}$. DOS is in [states/eV]. The vertical line is the Fermi level ($E_F = 0$).

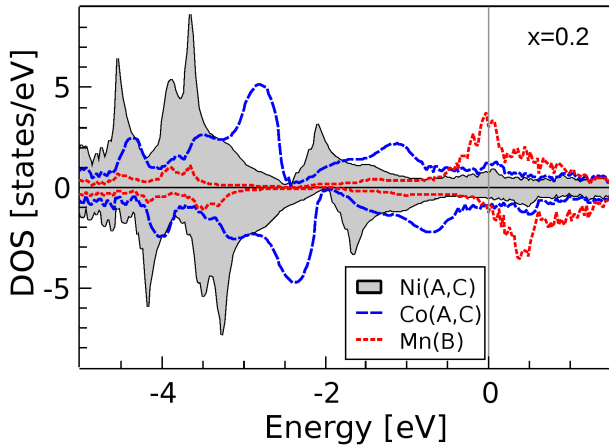


Fig. 2. The atom-resolved DOS in $\text{Ni}_{1.8}\text{Co}_{0.2}\text{MnGe}$. The vertical line is the Fermi level ($E_F = 0$).

We now turn our attention to the peak at E_F in the DOS of $\text{Ni}_{1.8}\text{Co}_{0.2}\text{MnGe}$. The structural instability of the cubic Heusler phase is typically indicated by such van Hove singularities at the Fermi level. One can expect that reasonable electronic relaxation mechanism, or magnetism, or a structural distortion reduce the DOS at E_F in $\text{Ni}_{1.8}\text{Co}_{0.2}\text{MnGe}$ (i.e. eliminate this singularity). Detailed analysis of the atomic resolved DOS of $\text{Ni}_{1.8}\text{Co}_{0.2}\text{MnGe}$ (Fig. 2) reveals that the contribution to the peak in the total DOS at E_F comes mainly from Mn(B). The atom-resolved DOS provide evidence that

electronic states of $3d$ Ni and $3d$ Co contribute to these peaks, also. However, it is clear that the overall trend in majority DOS at E_F for the system with $x = 0.2$ is dictated by $3d$ states of Mn(B). The unoccupied DOS at E_F and above derives mainly from the minority bands of Mn(B).

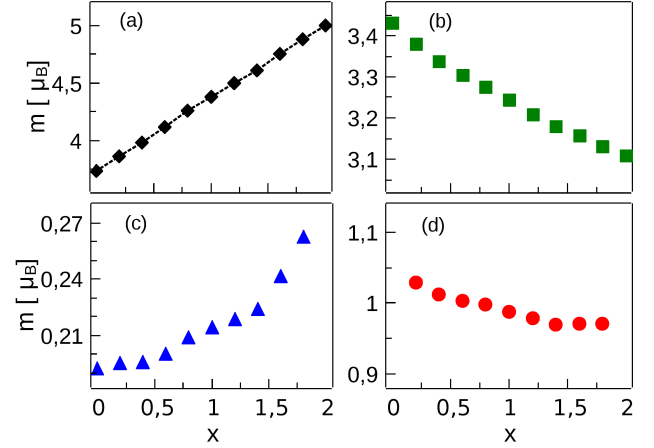


Fig. 3. Total magnetic moment (a) and contributions associated with individual atoms of Mn (b), Ni (c) and Co (d) in $\text{Ni}_{2-x}\text{Co}_x\text{MnGe}$ as a function of concentration x .

Every additional Co in A or C sites, as the first nearest neighbours of Mn(B), has effected to magnetic properties of Mn atom as well as other atoms. By increasing the concentration of Co atoms, the concentration of valence electrons decreases in the studied $\text{Ni}_{2-x}\text{Co}_x\text{MnGe}$, because Co has one electron less than Ni in its atomic orbitals. The linear growth of the total magnetic moment obtained in $\text{Ni}_{2-x}\text{Co}_x\text{MnGe}$ (Fig. 3) is in accordance with a Slater-Pauling type curve for the total spin-magnetic moment for binary alloys Ni-Co [13]. Most of the magnetic properties of the Heusler ferromagnetic alloys, like Ni_2MnGe or Co_2MnGe , stem from the magnetic moments of the Mn atoms. In the studied $\text{Ni}_{2-x}\text{Co}_x\text{MnGe}$ the Mn atoms are far from each other in the the cubic $L2_1$ structure, i.e. third nearest neighbor (NN) of each other regardless from Co concentration, which implies an indirect exchange mechanism. The calculated spin magnetic moments at Mn(B) are above $3 \mu_B$ in studied $\text{Ni}_{2-x}\text{Co}_x\text{MnGe}$ for the range of studied Co concentration. The values of Mn moment slightly decrease with x from $3.38 \mu_B$ for $x = 0.2$ to $3.13 \mu_B$ for $x = 1.8$. However, by Co substitution, the total magnetic moment increases which is due to the magnetic moment of Ni and Co atoms. The contributions of Ni to the magnetic moment modulates the overall trend dictated by Mn (due to its being largest), hence the total moment reflects a similar trend to that of Ni. The values of Ni moment obtained in our calculations ranges from $0.192 \mu_B$ for $x = 0$ to $0.262 \mu_B$ for $x = 1.8$. The Co moment changes from $1.028 \mu_B$ for $x = 0.2$ to $0.972 \mu_B$ for $x = 2.0$. A small negative magnetic moment ($-0.08 \mu_B \div -0.05 \mu_B$) is also induced on

Ge atom in the studied alloys. The calculated highest value of total magnetic moment of 4.999 μ_B is achieved for Co₂MnGe.

Structural properties of the studied Heusler compounds are computed by energy minimization procedure. The calculated total energy of the Ni_{2-x}Co_xMnGe as a function of unit cell volume (V) is fitted according to the Murnaghan isothermal equation of states (EOS) [14]:

$$E_{tot}(V) = E_0 + \frac{B_0 V}{B'(B' - 1)} \times \left[\left(\frac{V_0}{V} \right)^{B'} + B' \left(1 - \frac{V_0}{V} \right) - 1 \right], \quad (1)$$

where B_0 and B' are the bulk modulus and its pressure derivative at equilibrium volume V_0 . The computed structural parameters of Ni_{2-x}Co_xMnGe are given in Table I.

TABLE I

The calculated theoretical lattice parameter a_{th} corresponding to the minimum of the total energy, bulk modulus and its pressure derivatives for Ni_{2-x}Co_xMnGe

	a_{th} [Å]	B_0 [GPa]	B'
Ni _{1.8} Co _{0.2} MnGe	5.665	203 ± 2	1.6
Ni _{1.6} Co _{0.4} MnGe	5.659	198 ± 2	2.0
Ni _{1.4} Co _{0.6} MnGe	5.654	199 ± 2	2.5
Ni _{1.2} Co _{0.8} MnGe	5.648	208 ± 1	4.5
Ni _{1.0} Co _{1.0} MnGe	5.643	216 ± 1	3.5
Ni _{0.8} Co _{1.2} MnGe	5.637	218 ± 1	3.2
Ni _{0.6} Co _{1.4} MnGe	5.631	225 ± 1	3.7
Ni _{0.4} Co _{1.6} MnGe	5.625	230 ± 1	2.4
Ni _{0.2} Co _{1.8} MnGe	5.621	233 ± 1	3.0

4. Conclusions

To summarize, *ab initio* studies show that the Co substitution instead of Ni in parent Ni₂MnGe does not change magnetic ordering: the Ni_{2-x}Co_xMnGe remains ferromagnetically ordered. However, the total magnetic moment versus concentration x for Ni_{2-x}Co_xMnGe reveals an almost linear relationship. The electronic structure calculations of Ni_{1.8}Co_{0.2}MnGe exhibit a marked peaks in DOS at the Fermi level that may consider as a source of possible instability of the system. The calculated DOS for other compounds from series Ni_{2-x}Co_xMnGe with higher Co content have not any singularity in the DOS at E_F . Our study provides the values of bulk modulus and its pressure derivatives according to the isothermal EOS.

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