EPH - International Journal of Applied Science
ISSN (Online): 2208-2182
Volume 06 Issue 01 January 2020

DOI: https://doi.org/10.53555/eijas.v6i1.102

INVESTIGATION OF GEOMETRIC AND ELECTRONIC STRUCTURES OF HEUSLER ALLOYS: CUBIC AND TETRAGONAL LATTICES

T. Breczko[1], J. Tamuliene[2*], V. Barkaline[3]

Corresponding Author:-

Abstract:-

Ni_2MnGa and Co_2MnGa compounds were investigated by using state-of-the-art computational ab-initio methods. The total energy calculations for the cubic and the tetrahedral structures, band structure together with suspensibility investigations were performed. The results of our investigations exhibited the dependence of magnetic properties of the compounds on their geometrical structure. The influence of Co and Ni on the magnetic properties of the compounds was disclosed, too.

Keywords: - *Heusler alloys, ab-initio modeling, electronic structure*.

1. INTRODUCTION

Currently, ferromagnetic shape memory alloys have been extensively studied as potential candidates for smart materials. The possibility to use them in the spintronic-logic devices was also investigated. Among these materials, Ni_2MnGa is the most familiar alloy [Ullakko et.al (1996)]. The studies performed indicated that the material has a cubic L21 Heusler structure (space group Fm 3 m) with lattice parameter a = 5.825 Å at room temperature, and it acts as a ferromagnetic at the Curie temperature TC ≈ 365 K [Webster et al (1984); Brown et al. (2002)]. The Co_2MnGa alloys have acubic L21 lattice, high Curie temperature and spin polarization, too [Breczko, et al. (2010 and 2013)].

However, R. J. Kim et al. found a well-ordered crystalline, disordered and crystalline states with an intermediate order and exhibited the influence of structural order on physical properties of the Co_2MnGa and Ni_2MnGa derivatives [Kim et al (2006); Zayak al. (2013)]. Results of our investigations exhibited that the spin density of the Ni_2MnGa alloy are atomplacement-depended, i.e. magnetic and structural properties of the alloys is modified as the consequence of the atomic order change [Breczko et al. (2014); Sakon et al (2013)]. On the other hand, the interaction between magnetism and crystallographic rearrangements of the NiMn-Ga alloys is determined [Mañosa et al. (2008); Sánchez-Alarcos et al. (2008)]. Golub et al. performed the experiment to investigate the correlation between magnetic properties and a local structure in Ni–Mn–Ga systems [Golub et al. (2003)]. This experiment indicates the MnMn indirect exchange via the faults in Mn-Ga layers and shows that the exchange interaction between Mn-Mn magnetic moments is sensitive to the lattice transformation. It is also reported that Ni_2MnGa alloys martensitic transformation temperatures depend strongly on the alloy composition and electron atom ratio [Hosoda et al. (2002)].

The evolution of the structural ordering and crystal structure of polycrystalline Co_2MnGa films were studied by Kudryavtsev et.al. [Kudryavtsev et al (2007)]. The studies indicated that post annealing leads to the changes in the chemical and structural ordering from amorphous to more ordered structures typical for the Heusler alloys, and the magnetic properties vary correspondingly.

Moreover, our recent results obtained exhibited that the geometrical structure of the Ni compound could be more disordered than that of the Co one [Breczko and Tamuliene (2014)]. The calculated total isotropic susceptibility proves that the main difference between Ni_2MnGa and Co_2MnGa alloys could depended on the nature and location of an unpaired spin that leads to different forms of the magnetic field created by the alloy.

Hence, the question arises, what is the difference in electronic structure of the above alloys possessing different geometric structures. Thus, the purpose of our work is to simulate and explain the variety of structural properties of the Ni_2MnGa and Co_2MnGa compounds by using state-of-the-art computational ab-initio methods. The total energy for the cubic and tetrahedral structures, band structure and its nature and magnetizability are investigated. The results obtained could explain the dependence of magnetic properties of the alloys on the geometrical structure as well as the influence of Co and Ni on these properties.

2. Method applied

The quantum mechanical investigation of Ni_2MnGa and Co_2MnGa possessing cubic and tetrahedral structures were investigated by the Becke's three-parameter hybrid functional, applying the non-local correlation provided by Lee, Yang, and Parr (B3LYP) [Becke (1993)], – a representative standard DFT method LanL2DZ basis [Hay and Wadt (1985)]. The method and basis set were chosen so as to satisfy the two primary and competing criteria the accuracy and size, i.e., the method and the basis set should be suitable to describe the system under the tudy while computations should be performable.

The structures – crystal nanoparticles - under the study were optimized without any symmetry constraint. The magnetic susceptibilities were computed by using Gauge-Independent Atomic Orbital (GIAO) method because these calculations do not require large basis sets for achieving accurate results [Cheesemana nd et al. (1996)]. Gaussian 03 Rev D01 program package was applied here, too [Frisch, et al. (2003)].

3. Results obtained

Geometric structure

The differences of the structures of the Ni_2MnGa and Co_2MnGa compounds were described in paper [Tahuo Sakon 2013]. Here, we would like to remind the most important observations for exhibiting the main differences between the tetragonal and cubic structures of these compounds.

We have emphasized, that in the case of the cubic structure of the derivatives under the investigations, the elements of the L21 structure are possible to be obtained; the lattice parameters a, b, c are equal to ~ 3.0Å in the case of the structure with Ni, while with Co these parameters are equal to 2.97 Å; the cubic lattice planes are shifted in respect of one another in the case of Ni_2MnGa derivatives.

It is well known, that in tetrahedral molecular geometry, the central atom is located in the center with four substituents that are located in the corners of a tetrahedron. On the other hand, the geometry could be represented as a cube with a specific placement of the atoms making up the molecular structure. It leads to the presence of the edges consisting of the same atoms (in our case Ga or Mn) (Fig. 1). Hence, the main difference between the cubic and tetragonal structures of the compounds under the investigations concerns the edges. In the case mentioned of a cubic lattice the above edges are absent, while they are present in the case of a tetragonal structure. Hence, this simple observation allows us to describe geometric differences of the compounds under the investigation in respect of the cubic structure.

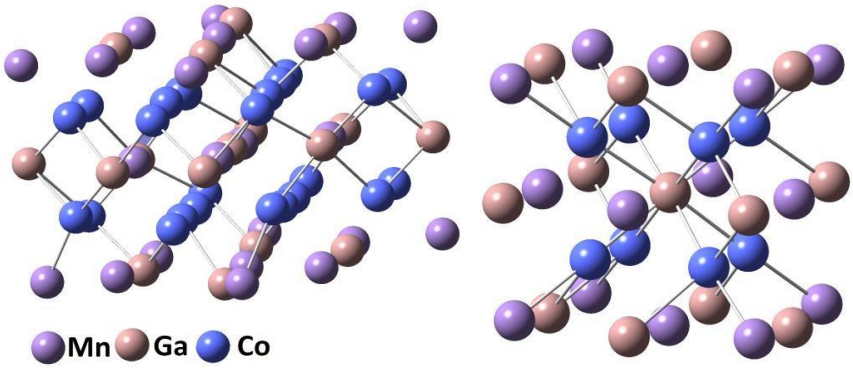

Figure 1: The tetragonal (on the left) and cubic (on the right) structures of the compounds under investigations

Remarkable structural distortions are obtained in the case of the tetragonal lattice. It is necessary to mention that the cubic placement of the Mn and Ga atoms is disordered in both Ni and Co compounds (Fig. 1). In these compounds, the Mn and Ga atoms form rhombohedra the parameters of which are placed in Table 1.

Table 1: Parameters of the lattice of the compounds under the investigation presented in Å and degrees

Compound	a	b	c	**α**	**β**	**Γ**
Ni_2MnGa	3.1	2.9	2.9	87	88	97
Co_2MnGa	3.3	2.8	2.8	91	87	91

The comparison of the lattice parameters of cubic and tetragonal structures indicates the significant changes of the lattice angles in the case of the Ni compounds. When speaking about the Co compounds, a significant elongation in the lattice length together with the decrease of one of the lattice angles is observed.
The distance between the atoms (Ni or Co) located in the centre of the lattice varies from from 2.7 Å to 3.4 Å, while the dihedral angles of the structures formed by these atoms are in the range of [83.06; 89.76] and [85.93; 96.39] for the Ni and Co compounds respectively. Referring to the results we predict, that primitive lattices are shifted in tetragonal structures. Moreover, the shift in Co_2MnGa is larger than that in the Ni_2MnGa, although in the cubic structure of the Co compound the shift was not observed.
The thermal stability of the compounds undoubtfully depends on their geometric structure. To evaluate which compounds under the investigation are thermally more stable, the binding energies per atom are calculated. Referring to the results obtained us could state:

- the compounds possessing cubic lattices are more stable than those with the tetragonal lattice;
- The Ni_2MnGa compounds are more stable than the Co_2MnGa ones in both cubic and tetragonal lattice cases.

It interesting to mention, that the binding energy per atom of Ni_2MnGa in the case of both cubic and tetragonal lattices is 0.4 eV larger than that of Co_2MnGa. Moreover, the shapes of our compounds investigated are similar. Hence, referring to the results described, we could speculate that the phase transition temperature is electronic- , but not geometric-structure dependent, i.e. the transition temperature is dependent on the nature of chemical bonds formed.

3.1. Electronic structure

Let us remember that semimetals possess electrons on Fermi level with spins up or down, i.e. the electron spins on the Fermi level are not compensated. Thus the densities of the states (DOS) of electrons with different spins are different what leads to the appearance of the gap of DOS at the Fermi level. These gaps are present in all compounds under the investigation (Fig. 2-5).

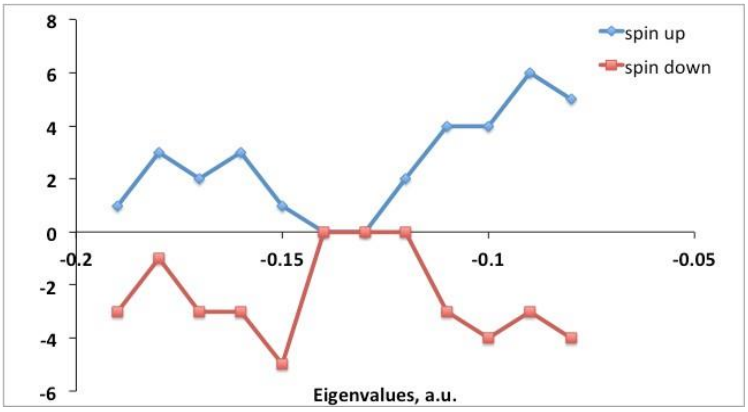

Figure 2: Density of the state with a spin up and down of the Ni_2MnGa compound with a cubic lattice

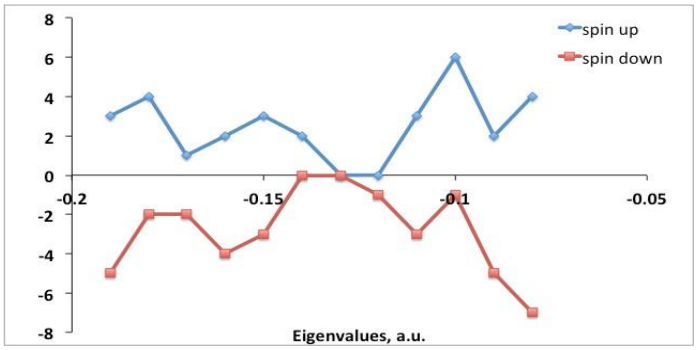

Figure 3: Density of the state with a spin up and down of the Co_2MnGa compound with a cubic lattice

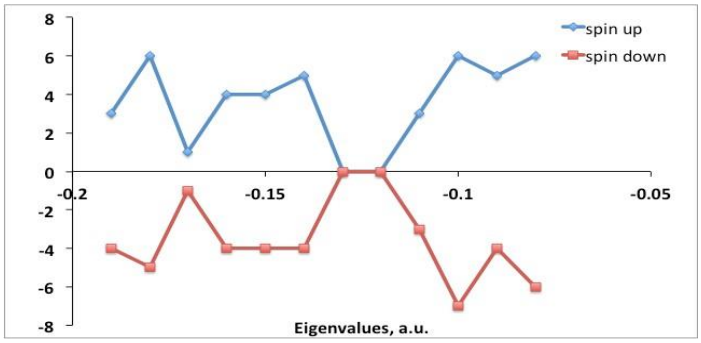

Figure 4: Density of the state with a spin up and down of the Ni_2MnGa compound with a tetragonal lattice

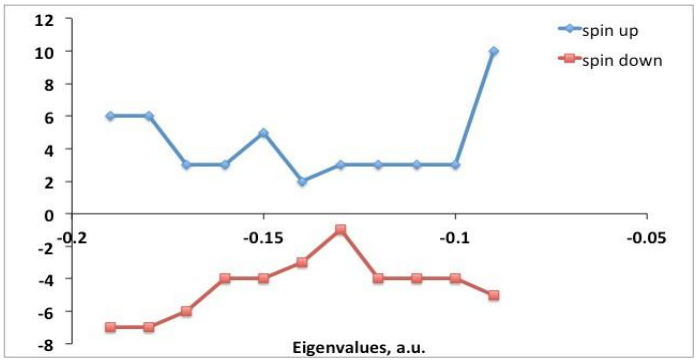

Figure 5: Density of the state with a spin up and down of the Co_2MnGa compound with a tetragonal lattice

The DOS analysis also indicates that the Ni_2MnGa compounds with cubic and tetragonal lattices are semiconductors. The properties of the Co_2MnGa are lattice- dependent: the compounds are semiconductors when the lattice is cubic, and semimetals when it is tetragonal.

It is no doubt, that the compounds under the investigation are a paramagnetic, what is confirmed by the presence of the unpaired electron as well as spin gaps in DOS. The results of the isotropic total susceptibility calculations confirm this prediction (Table 2).

Table 2: Isotropic total susceptibility of the compounds under the investigation. The value of suspensibility is divided from the number of compounds to avoid the parameter dependence on the size of the compounds

Compound	Cubic lattice	Tetragonal lattice,
Ni_2MnGa	22.60	92.77
Co_2MnGa	22.53	132.25

It is evident that the values of suspensibility of the compounds with a tetragonal lattice are larger than those of the compounds with the cubic lattice. (Table 2) These results coincide with the experimental observations of $Ni_{2.+x}Mn_{1-x}Ga$ and $Ni_{2.+x}Mn_{1-x}Ga$ obtained by T. Breczko et al. [Breczko et al. (2007)] The results of the above authors show the increasing of magnetic suspensibility of these compounds from 0.2 -0.5 arb. Units to 1.0 arb. Units within the 280-350 K temperature range [Breczko et al. (2007)]. These observations allow us to speculate that the lattice of the Ni_2Mn Ga and Co_2MnGa compounds could transform within the 280-350 K temperature range, i.e. the cubic lattice becomes the tetragonal one due to the shift of the lattice planes in respect of one another.

Conclusions

We simulated and explained the variety of structural properties of the Ni_2MnGa and Co_2MnGa compounds by using state-of-the-art computational ab-initio methods. Referring to the results obtained we state that the compounds possessing the

cubic lattices are more stable than those with the tetragonal lattices. Moreover, the Ni_2MnGa compounds are more stable than the Co_2MnGa ones in both cubic and tetragonal lattice cases.
We obtained that the Ni_2MnGa compounds with cubic and tetragonal lattices are semiconductors. The Co_2MnGa compounds with cubic lattices are semiconductors, too while those with the tetragonal ones are semimetals.
It is no doubt, that the compounds under the investigation are paramagnetic.
Larger values of suspensibility of the compounds with tetragonal lattice were obtained. Moreover, we speculate that the lattices of the Ni_2Mn Ga and Co_2MnGa compounds could transform within the temperature range of 280-350 K, i.e. a cubic lattice becomes a tetragonal one due to the shift of the lattice planes in respect of one another within the temperature range mentioned.

Acknowledgments
The authors greatly appreciate the contribution of the Supercomputing centre of MIF of the University of Vilnius for resources and support provided. The computations were carried out at the Computer Center of University of Bialystok, too. The work is supported by TAP-LB14-011 project.

References
[1].**Ullakko, K.; Huang, J.K.; Kantner, C.; O'Handley, R.C.; Kokorin, V.V**. (1996) Large magnetic-field-induced strains in Ni_2MnGa single crystals: Appl. Phys. Lett. Vol. 69, p.p.1966–1968.
[2].**Webster, P.J.; Ziebeck, K.R.A.; Town, S.L.; Peak, M.S. (1984)** Magnetic order and phase transformation in Ni_2MnGa: Philos. Mag. B vol. 49, p.p. 295–310.
[3].**Brown, P.J.; Crangle, J.; Kanomata, T.; Matsumoto, M.; Neumann, K-.U.; Ouladdiaf, B.; Ziebeck, K.R.A**. (2002) The crystal structure and phase transitions of the magnetic shape memory compound Ni_2MnGa: J. Phys. Condens. Matter. vol. 14, p.p. 10159–10171. **Breczko, T;, V.V. Barkaline , V.V.; Grechishkin, R.M.; Nelayev, V.V**.(2010): Magnetic properties of Ni_2MnGa alloy. Materials Physics and Mechanics vol. 9 p.p. 53-67.
[4].**Breczko, T.; Barkaline, V.V.; Douhaya**, Y. (2013) Modeling of smart material properties of Heusler alloys: Material Science Forum vol. 738-739, pp 426-430.
[5].**Kim, R.J; Yoo,Y. J.; Yu, K.K.; Nahm, T.U.; Lee, Y.P.; Kudyavtsev, Y.V.; Oksenenko, Y.V.; Rhee, J.Y.; Kim, K.W. (2006):** Structural Dependence of the Physical Properties for Co_2MnGa Heusler Alloy Films .Journal of the Korean Physical Society, vol. 49, 3, p.p. 99 1000.
[6].**Zayak, A.T** (2003) Ph.D. thesis 'A first-principles investigation of the magnetic, structural and dynamical properties of Ni_2MnGa'
[7].**Breczko, T.; J. Tamuliene, J.** (2014): Investigation of electronic properties of Ni_2MnGa, and Co_2MnGa Heusler alloys. Materials Physics and Mechanics, vol. 20 p.p. 37-43.
[8].**Takuo Sakon, Yoshiya Adachi and Takeshi Kanomata,** Magneto-Structural Properties of Ni2MnGa Ferromagnetic Shape Memory Alloy in Magnetic Fields, Metals 2013, 3, 202-224; doi:10.3390/met3020202
[9].**Mañosa, L.; Moya, X.; Planes, A.; Krenke, T.; Acet, M.; Wassermann, E.F.** (2008): NiMn-based magnetic shape memory alloys: Magnetic properties and martensite transformation. Mater. Sci. Eng. A, vol. 481–482, p.p. 49–56.
[10]. **Sánchez-Alarcos, V.; Pérez-Landazábal, J.I.; Gómez-Polo, C.; Recarte, V.** (2008) Influence of the atomic order on the magnetic characteristics of a Ni–Mn–Ga ferromagnetic shape memory alloy. J. Magn.Magn. Mater. , vol. 320, p.p. e160–e163.
[11]. **Golub, V.O.; Vovk, A.Y.; O'Connor, C.J.; Kotov, V.V.; Yakovenko, P.G.; Ullakko, K.** (2003) Magnetic and structural properties of nonstoichiometric Ni_2MnGa alloys with Ni and Ga excess. J. Appl. Phys., vol. 93, p.p. 8504–8506.
[12]. **Hosoda, H; Wakashimas, K.; Sugimoto, T.; Miyazaki, S. (2002):** Hardness and agnig of Ni2MnGa ferromagnetic shape memory alloys. Materials Transactions, vol. 43, 5, p.p. 852 855.
[13]. **Kudryavtsev, Y.V.; Oksenenko, V.A.; Lee, Y.P.; Hyun, Y.H.; Kim, J.B.; Park, J.S.; Park, S.Y.** (2007): Evolution of the magnetic properties of Co_2MnGa Heusler alloy films:From amorphous to ordered films. Physical review b, vol. 76, p.p. 024430 – (1-9).
[14]. **Becke A.D. (1993):** Density-functional thermochemistry. III. The role of exact exchange J. Chem. Phys. vol. 98, p.p. 5648.
[15]. **Hay, P.J.; Wadt, W.R**. (1985): Ab initio effective core potentials for molecular calculations potentials for K to Au including the outermost core orbitals. J. Chem. Phys., vol. 82, p.p. 299-310.
[16]. **Cheeseman, J.R.; Trucks, G. W.; Keith, T. A.; Frisch, M.J.** (1996): A Comparison of Models for Calculating Nuclear Magnetic Resonance Shielding Tensors, J. Chem. Phys., vol. 104, p.p. 5497-509.
[17]. **Frisch, M. J.** (2003) , Gaussian 03 (Gaussian, Inc., Wallingford, CT).
[18]. **Breczko, T.; Bykov, D.; Grechishkin, R.; Zalytov, A.; Ilyashenko, S.; Bramowicz, M.** (2007): Martensite and magnetic doman structure of mono-, poly- and nano-crystaline feromagnetic shape memory alloys, Proceedings of SPAS, vol.11, p . .pp. 113081 -113086.