

INVESTIGATION OF ELECTRONIC PROPERTIES OF Ni₂MnGa AND Co₂MnGa HEUSLER ALLOYS

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Abstract. The work is devoted to the Heusler alloys as a candidate for applications in spintronics. On the basis of experimental studies the electronic structures of these alloys by computer simulations were carried out to explain the structural and electronic properties of the Ni₂MnGa and Co₂MnGa compounds by using state-of-the-art computational ab-initio methods. The total energy calculations for the cubic structures, band structure and their nature and magnetizability of the compounds are investigated. The obtained results explained the dependence of the magnetic properties of the alloys on the geometrical structure as well influence of Co and Ni atoms.

1. Introduction

Half-metallic ferromagnetic alloys have been studied as candidates for the metal-based spintronic-logic devices. Among many half-metallic ferromagnetic materials special attention was paid to Heusler alloys such as Ni₂MnGa and Co₂MnGa that show high Curie temperature and high spin polarization [1-5]. Several studies by means of X-ray and neutron diffraction measurements indicate that the alloys present L2₁ structures with mainly ferromagnetic ordering [6]. However, R. J. Kim and et al. found a well-ordered crystalline state, a disordered state, and crystalline state with an intermediate order and exhibited influence of structural order on physical properties of Co₂MnGa films [7]. The similar phenomena for the Ni₂MnGa are described in work [8]. More often, the substrate temperature is mentioned as having dramatic effects on the structural ordering and magnetic properties; however the effects of structural disorder on various physical properties of these alloys are not fully understood. Moreover, the dependence of electronic structure on the alloy geometrical structure is insufficiently described although it could be the main reason for understanding what can be responsible for many of the alloy properties.

Hence, the purpose of our work is to simulate and to exhibit differences of Co₂MnGa and Ni₂MnGa compounds by using state-of-the-art computational ab-initio methods. Calculations of total energy and magnetizability for cubic structures are done. We hope that the results obtained will explain the influence of Co and Ni on magnetic properties of the compounds.

2. Method applied

In the density functional theory, both the complicated many-electron wave functions and the respected Schrödinger equation are replaced by a much simpler electron density function $\rho(r)$ and by a new calculation pathway. The above mentioned replacement is based on the Hohenberg-Kohn theorem [10]. In many cases the results of DFT calculations for solid-

where ε_l are Lagrange multipliers. The numerical potentials are fitted analytically by Gaussian functions.

Contracted “double-zeta” [2s2p2d] basis set is obtained by leaving the outermost function uncontracted and by contracting the remaining inner functions into a single function. The exponents of the (5d) primitive functions for the 3d orbits are taken directly from Rappaport and et al. [12]. The effective potential should provide accurate results for transition metal compounds comparable to ab initio all-electron calculations on the same systems and for a small fraction of the computational cost. However, it is necessary to take into account that spin densities obtained with basis sets that replace the core electrons by pseudopotentials should be taken with caution although the calculated spin densities are relatively insensitive to the quality of the basis set. It is necessary to mention that most of the spin density distribution data can be understood qualitatively in simple terms, by taking into account the theoretical foundations of the two electron interactions that determine the spatial distribution of the electrons in molecule.

3. Results and discussion

The structures of Ni_2MnGa and Co_2MnGa having $L2_1$ structure are shown in Fig. 1. It is necessary to mention, that geometry optimization of the both structure is performed with the requirement to keep symmetry. Additionally, the structures investigated are modeled in such a way that they could represent nano-crystal, but not crystal, i.e. the boundary conditions are not involved in the study. The aim of the first investigation is to propose how the electronic properties of the alloys could be changed when Ni atoms in the lattice are changed by the Co atoms and vice versa.

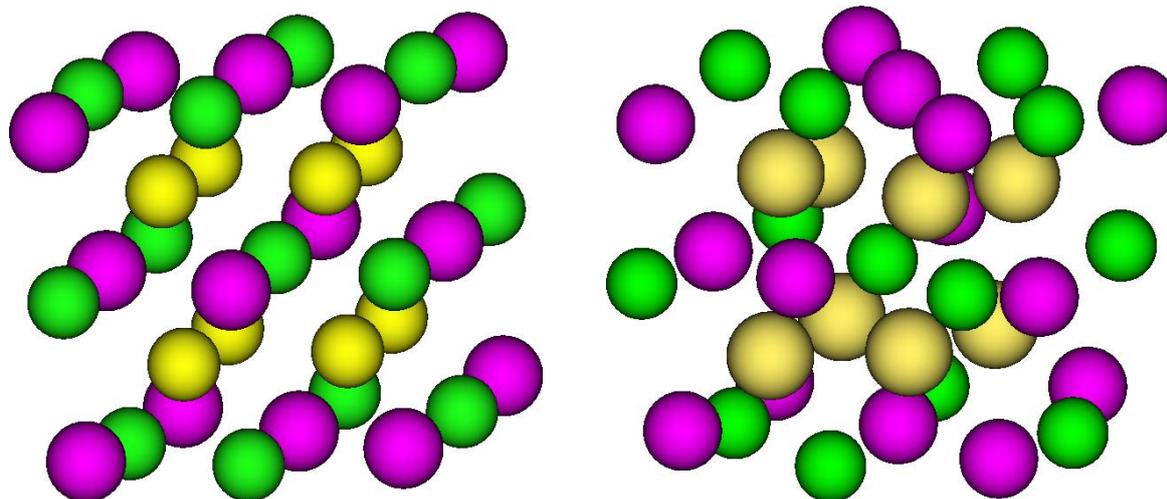


Fig. 1. Co_2MnGa structure on the left and Ni_2MnGa structure on the right. Co or Ni atoms are marked by yellow spheres, Ga by green, Mn by fuchsia.

Results of the first investigations indicate that the geometrical structure of Ni_2MnGa could be more disordered than that of Co_2MnGa although the elements of $L2_1$ structure could be obtained in both compound investigated. The lattice parameters a , b , c is equal to $\sim 3.0 \text{ \AA}$ for the structure with Ni, whereas they are equal to 2.97 \AA for the structure with Co. Hence, there is no remarkable difference between geometrical structures of the lattice of the compound investigated. However, the difference occurs in the compound investigated consisting of several lattices.

First, it is necessary to pay attention that Co atoms inside the structure investigated located at the cube corner. Co-Co bond length is equal to 2.9 \AA , while Co-Co-Co angle is

orbital such as half-filled HOMO) of Mn and Ga atoms overlap slightly and that allow us to ignore the above facts on electronegativity of the atoms, because when two SOMOs come together and overlap, there is a dramatic stabilization of two electrons. The atoms will react by forming a bond between two SOMOs. Taking into account that SOMO of Mn atoms lie low (-0.14 a.u) than that of Ga (-0.13 a.u) we may foresee that the electron located on half filled orbital of Mn atoms and this is a main reason while Mn possess negative charge in our investigated compound, and Ga atom charges are positive (Fig. 2). On the other hand, an additional electron is located on Mn atoms mostly due to their configuration of d orbital [18]. It is necessary to remember that only Mn atom could have oxidative state such as -1, -2 or -3, while for other atoms of the compounds the oxidative state is positive; it indicates that these atoms cannot accept an additional electron.

However, despite the different Mulliken atomic charges calculated and slightly different geometrical structures, the charge distributions are quite similar that is indicated by calculated dipole moment and its direction. The dipole moment of Co_2MnGa is equal to 1.25 Debye, while that of Ni_2MnGa equals 1.18 Debye. Moreover, in both case it is possible to recognize one dominant and satellite directions, which component value is approximately two times smaller (Table 1).

Table 1. Dipole moment (field-independent basis, Debye) of Co_2MnGa and Ni_2MnGa compounds.

Compound	dx	dy	Dz	Total
Co_2MnGa	-0.61	-0.33	1.03	1.25
Ni_2MnGA	1.00	0.35	0.52	1.18

The dipole moment indicates electron concentration sites in the structure. On the other hand, the components of these dipole moments allow us to foresee distribution of the above sites. Both the concentration of electrons and their distribution helped us to find additional spins that appeared due to different oxidation state of the atoms (formally we call the above spin as an ion one). The spin can also influence on magnetic properties of the structure investigated [19]. Taking into account, that for both compounds the satellite component of the dipole moment is obtained, we can predict that the additional spin takes place and influences magnetic properties of the structures investigated. The prediction supports the observation of different condensation of electrons on atoms indicating triple, double and single bonds between different atoms. However, the later investigation proves that the main spin occurs due to odd number of Mn atoms and the above spin does not influence on magnetic properties of the compound.

It is known that there are two mechanisms through which an unpaired d electron of a transition metal ion can place some spin density at other atoms of a molecule, as well as at its own other atomic orbitals [20]. On one hand, the molecular orbital that hosts an unpaired electron, even if with major contribution from the metal d orbital, mixes in the atomic orbitals of donor atoms. Hence, the electron delocalization results in a distribution of positive spin density throughout the molecule determined by the composition of the SOMO. As we mentioned above, the resulting distribution of spin density is arisen from a spin delocalization and is related with electrons distributions too. Summing up the spin densities of different atomic orbitals of an atom, one obtains the corresponding atomic spin density. The second way through which an unpaired d electron of a transition metal ion can place some spin density at other atoms of a molecule is the spin polarization mechanism. The spin of a bonding electron pair is polarized in such a way that the positive spin is concentrated close to the atom that has an unpaired electron, where a concentration of negative spin density is

avored around the atoms bonded to it [20]. Hence, the atomic orbitals contribution to SOMO studied discovers the largest portions of the spins as well as the Milliken atomic spin densities.

The investigation of the composition of the SOMO exhibited that the orbital consists mostly of d orbitals of Mn atoms for both structures investigated slightly mixed with those of Ni or Co atoms. Additional analysis of the Milliken atomic spin density allows us to determine that the spin is concentrated on Mn atoms, i.e. the largest spin densities are obtained on Mn atoms. It is necessary to pay attention to different spin densities (up and down) on Mn atoms located in different sites of the investigated compound. However the main difference between Co_2MnGa and Ni_2MnGa appears when total spin densities on certain atoms are investigated. In the case of Co_2MnGa , the positive spin density is located on Ga atom, while that in the case of Ni_2MnGa is on Mn atom. By the way, it is necessary mention that the last results obtained coincide with those obtained earlier by us with the help of semi empirical methods. It implies that spin polarization is a way, through which the positive spin at the paramagnetic centre may induce some spin density of the opposite sign at the atoms bonded to it.

For this reason, the atomic spin density was analyzed too. The analysis exhibits that in Ni_2MnGa compound, the largest positive spin is located on Ni-Mn bonds. Hence, the spin of a bonding electron pair is polarized in such a way that the positive spin is concentrated close to the atom that has unpaired electrons, whereas a concentration of a negative spin density is favored around the atom bonded to it. It implies that the combination of spin delocalization and spin polarization results in a such spin density distribution that the positive spin is located mainly on Mn atoms. In the case of Co_2MnGa compound, the largest positive spin is located on Co-Co bond that consist atoms having unpaired electrons. As results, the polarized spin is delocalized, the spin up and down located on Mn atoms and Co atoms which number is even, quenched and non-compensate spin is located on Ga atoms which number is odd.

The magnetic properties of these two compounds are similar despite of their different nature. It is indicative by the fact that the isotropic total susceptibility calculated is equal to 788.51 and 791.18 for Co_2MnGa and Ni_2MnGa , respectively. Hence, the main difference between Ni_2MnGa and Co_2MnGa alloys is the nature and location of the unpaired spin that leads to different form of the magnetic field created by the compound.

4. Conclusion

To clear up how electronic properties of Heusler alloys could be changed when Ni atoms in their lattice are changed by Co atoms and vice versa, computer simulations were carried out. Results obtained exhibited that the geometrical structure of the Ni compound could be more disordered than that of the Co ones. The analysis of all the electrons condense to atom indicates different electronic structures, i.e. Ni atoms forms triple or double bonds with Mn and Ga, while in Co alloys there is no bonds that are formed by different kind atoms, e.g. Co and Mn. However, despite of the different geometric and electronic structures, the charge distribution in the investigated compounds is quite similar. The dipole moments calculated give an indication of it. We have found the dominant and satellite directions of the dipole moment components in both alloys, but we have found no influence on magnetic properties of the alloys.

We determined the largest positive spin location on Ni-Mn bonds by analyzing the atomic spin density and concluded that the positive spin could locate mainly on Mn atoms in Ni_2MnGa alloy. In the case of Co_2MnGa alloy, the largest positive spin location is on Co-Co bond. The polarized spin is delocalized, the spin up and down located on Mn atoms and Co atoms, which number is even, quenched and non-compensate spin is located on Ga atoms, that number is odd.

The calculated isotropic total susceptibility proves that the main difference between Ni₂MnGa and Co₂MnGa alloys could be of the nature and location of an unpaired spin that leads to different forms of the magnetic field created by the alloy.

References

- [1] S. Fujii, S. Sugimura, S. Ishida, S. Asano // *Journal of Physics: Condensed Matter* **2** (1990) 8583.
- [2] T.M. Breczko, V. Nelayev, K. Dovzik, M. Najbuk, M. Bramowicz // *Proceedings of SPIE* **7377** (2008).
- [3] T. Breczko, V.V. Barcaline, Ya.V. Douhaya, In: *Phase Transitions and Strength of the Crystals, 6 Conf.* (Черноголовка, 2010), p. 79 (in Russian).
- [4] T. Breczko, V.V. Barcaline, R.M. Grechishkin, V.V. Nelayev // *Materials Physics and Mechanics* **9** (2010) 53.
- [5] T. Breczko, V.V. Barcaline, Ya.V. Douhaya // *Material Science Forum* **738-739** (2013) 426.
- [6] A. Ayuela, J. Enkovaara, K. Ullakko, R. M. Nieminen // *Journal of Physics: Condensed Matter* **11** (1999) 2017.
- [7] R.J. Kim, Y.J. Yoo, K.K. Yu, T.U. Nahm, Y.P. Lee, Y.V. Kudyavtsev, Oksenenko, J.Y. Rhee, K.W. Kim // *Journal of the Korean Physical Society* **49** (2006) 996.
- [8]. Alexey T. Zayak, *A first-principles investigation of the magnetic structural and dynamical properties of Ni₂MnGa*, Ph.D. thesis (Duisburg-Essen, Germany, 2003).
- [9] A.D. Becke // *The Journal of Chemical Physics* **98** (1993) 5648.
- [11] P.A. Christiansen, Y.S. Lee, K. Pitzer // *The Journal of Chemical Physics* **71** (1979) 4445.
- [12] A.K. Rappe, T. Smedley, W.A. Oddrd III // *The Journal of Chemical Physics* **85** (1981) 2607.
- [13] <http://www.webelements.com>.
- [14] R.H. Petrucci, W.S. Harwood, G. Herring, *General Chemistry: Principles and Modern Applications* (Prentice–Hall, 2002).
- [15] NIST Atomic Spectrum Database.
- [16] G.L. Miessler, D.A. Tarr, *Inorganic Chemistry* (Prentice–Hall, 1999).
- [17] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements* (Pergamon, 1984).
- [18] S.E. Kulikova, S.V. Eremeev, T. Kakehita, S.S. Kulikov, G.E. Rudenski // *Materials Transactions* **47** (2006) 599.
- [19] J. Tamulienė, R. Vaišnoras, G. Badenes, L.-M. Balevičius // *Journal of Nanomaterials* **2009** (2009) ID 308276.
- [20] E. Ruiz, J. Cirera, S. Alvazer // *Coordination Chemistry Reviews* **249** (2005) 2649.