Theoretical Investigations of the Structural, Magnetic and Electronic Properties of F$_{2-x}$MnGe:Cu$_x$ Alloy

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The paper presents results of theoretical investigations on the structural, magnetic and electronic properties of Fe$_{2-x}$MnGe:Cux Heusler alloy focusing on the role of iron-copper substitution effects on selected parameters. The calculations were performed on the basis of the density functional theory approach using the plane-wave basis set. The substitution of [Ar]4s1 3d10 copper in place of [Ar]4s2 3d6 iron site was investigated.Among the many interesting properties exhibited by those alloys such as shape memory effect, half-metallicity, magnetoresistance etc. they also demonstrate significant sensitivity to various doping affecting their magnetic characteristics such as magnetic ordering or total magnetic moment, often demonstrating the Slater-Pauling behaviour. The Cu substitution caused break of half-metallic character at the same time resulted in increase of magnetization.

Keywords: Density functional theory, Heusler alloys, magnetic properties, electronic properties, ab initio

The X_2YZ type Heusler alloys are being studied for about three decades and the interest in these compounds continues due to their remarkable properties such as magnetic ordering, half metallic character (HM), magnetocaloric and often shape memory effects [1-6].

One of the most interesting groups of these compounds is the half-metallic group, which presents effect of total spin polarization. This effect is caused by one of electron spin bands which while crossing the Fermi level (E_F) has a band gap (like semiconductor), while the second one remains fully metallic. Thus, electric current passing thru material can be totally polarized. The creation of minority band gap is related to the d orbital hybridization between transition metals forming the structure of material, assisted by sp - element which because of bigger electronegativity can be considered as electron hole [7]. The density of states (DOS) near E_F at different atoms leads to a different hybridization of majority and minority spins. Therefore a gap in the minority band arises and due to sp - element presence a shift in majority band is observed, leading to its metallic behavior.

The half metallic ferromagnets (HMF) of X_2YZ type often crystallize in $L2_1$ structure (Fm-3m space group, no. 225) where X and Y atoms are d - orbital transition metal block atoms and Z is an sp - orbital element [8,9]. Among many types of structures, those that are consisted of Fe and Mn atoms together with sp elements like Si, Ge, Ga, Al or Sn often exhibit desirable half-metallic properties. At the same time, even small addition/substitution of d block elements can influence both HM and magnetic properties significantly [10]. The full understanding of the interactions taking place between substituted structure elements is therefore necessity both from a purely scientific point of view as well as from the applications point [11-14].

In this paper the influence on structural, magnetic and electronic properties of Fe_2MnGe Heusler alloy with Fe element substituted by Cu are investigated using *ab initio* calculations.

Computational details

The calculations were done using Quantum Espresso [15] software package utilizing density functional theory (DFT) *ab initio* approach. The cubic $L2_1$ ordered structure with Mn in (0,0,0), Ge in (1/2, 1/2, 1/2) and Fe in (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4) was used [6-8]. The Cu substituted one Fe atom at (1/4, 1/4 3/4) site. For all calculations we used PAW - ultrasoft pseudopotentials with starting electron configurations of [Ar] $4s^2\,3d^6\,4p^0$ for Fe, [Ar] $4S^2\,3d^5$ for Mn, [Ar] $4s^1\,3d^{10}\,4p^0$ for Cu and [Ar] $4s^2\,3d^{10}\,4p^2$ for Ge elements. Each pseudopotential included scalar relativistic effects, with nonlinear core corrections. The generalized gradient approximation (GGA) in the Perdew, Burke and Ernzerhof (PBE) [16] form were used. As it is known the GGA:PBE approach can underestimate the band gap, nevertheless despite drawbacks, GGA has a number of other advantages (like structure or magnetism predictions), so following the approach from works [6-8] we used it to preserve the possibility of direct results comparison. We also did not include the spin-orbit coupling. Before any calculation convergence tests were conducted. Based on those tests, we established a 12x12x12 k-points mesh (using Monkhorst-Pack scheme [17]) Brilouin zone sampling for SCF and 24x24x24 for DOS calculations, wavefunctions kinetic energy cutoff *ecutwfc=68* Ry and *ecutrho=790* Ry for charge density cutoff. Also for convergence acceleration we used conventional Gaussian smearing of Fermi surface with value of 0.02 Ry. The electronic convergence criteria was set to 10^{-7} Ry.

The first step was to find $L2_1$ structure equilibrium lattice parameter *a*. In order to optimize this parameter a Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm was utilized, ensuring the force convergence criteria for ionic minimization lower than $1x10^{-3}$ a.u.. Then, one Fe atom was replaced by Cu and the energy minimization procedure was repeated for second structure. Due to crystal symmetry all sites occupied by Fe are equivalent. Computations included magnetic moment per site taking into account collinear magnetism (ferromagnetic ordering)

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[18]. According to this, spin up and down were treated separately. The translational asymmetric unit cell consisted of 16 atomic positions. The unit cell (including atoms periodic boundary copies) is shown in figure 1. Structural parameters were obtained both for nonmagnetic and ferromagnetic configurations.

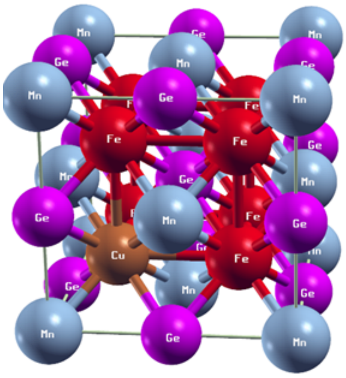

Fig. 1. Structure of Fe_2MnGe:Cu Heusler compound. The Fe_2MnGe structure is identical (with Fe in place of Cu atom)

Results and discussions

Table 1 shows structural parameters calculated for three compounds: Fe_2MnGe in non magnetic state, the same structure in ferromagnetic state and structure with Cu substitution with ferromagnetic state. As can be seen, the nonmagnetic cell volume is bigger than in the case when magnetism is included in calculations. The given calculated structure parameters are in well agreement with other papers [6-9,19].

In comparison between substituted and starting magnetic structures, the size of cell increases with Cu substitution what is expected due to bigger metallic radius of Cu atom compared to Fe (128 pm vs 126 pm respectively). As a result, the Fe-Fe distances were also increased. The calculated change in volume between these structures is 3.9 Å^3. Because Fe_2MnGe is ferromagnetic [6-8, 19], and lower total energy criteria is met for FM ordering, in the following part we will consider only collinear magnetic case of presented Heusler structure.

Electronic structure

As can be seen in figure 2, major contribution to the DOS both in starting structure and structure with Cu substitution (fig. 3) comes from iron atoms. The spin polarization in first case is ~98%, similar in [6]. The second largest contribution comes from Mn atoms causing their hybridization in nearly whole range, from about -6 eV below E_f up to 3 eV above E_f. Both determine properties at the Fermi level and decide about metallic character of majority spin band. Germanium atoms have minor contribution to the DOS at E_f.

There is a clearly visible effect of the Cu substitution on the DOS (fig. 3). This breaks down the half metallic character of minority spin band and generally lowers the DOS amplitude. However, there is no evidence of Cu orbital hybridization at E_f in the minority band. Instead, the states at E_f of minority channel rise mainly due to the iron contribution, as it shifts toward higher energies. Cu provides two more electrons in respect to Fe. Interestingly its contribution to DOS reveals between -5 eV and -2 eV, so in lower lying energy states. The copper 3d shell is closed, and only 4s electron is unpaired. Thus, nearby Fe ions that previously were bonded with substituted Fe, now have more unbounded electrons, that are giving rise of minority DOS channel at E_f.

Table 1
CALCULATED STRUCTURAL PARAMETERS

Structure	a [Å]	V [Å^3]	Fe-Fe [Å]
Fe_2MnGe - nonmag.	5.745	189.68	2.872
Fe_2MnGe - FM mag.	5.689	184.13	2.844
Fe_2MnGe:Cu - FM mag.	5.729	188.03	2.864
Fe_2MnGe [6]	5.682	-	-
Fe_2MnGe [7]	5.700	-	-
Fe_2MnGe [9] - EXP.	5.781	193.21	-
Fe_2MnGe [19]	5.780	-	-

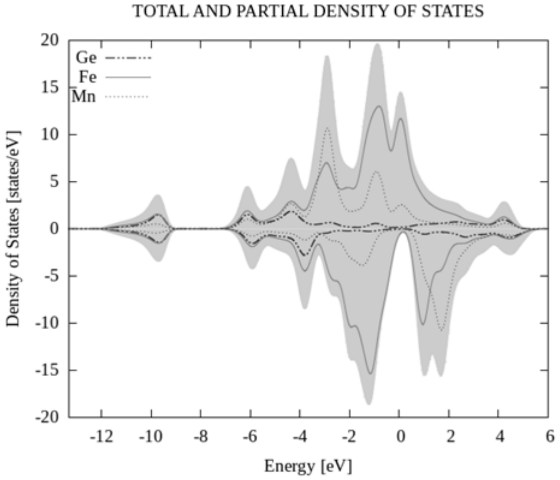

Fig. 2. Total (solid) and partial (lines) density of state for Fe_2MnGe. Zero denotes Fermi energy

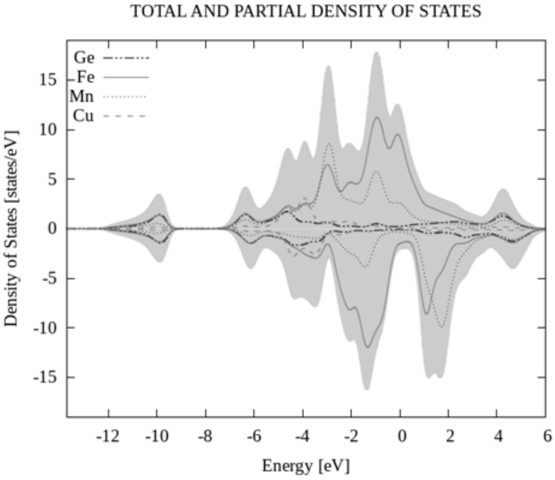

Fig. 3. Total (solid) and partial (lines) density of state for Fe_2MnGe:Cu. Zero denotes Fermi energy.

Table 2
UNIT CELL MAGNETIC PROPERTIES

Structure	Total magnetization [µB/Cell]	Absolute magnetization [µB/Cell]	Tot-Abs [µB/Cell]
Fe_2MnGe	12.18	14.78	-2.60
Fe_2MnGe:Cu	13.53	15.65	-2.12

Magnetic properties

The Fe_2MnGe is ferromagnetic and the substitution by Cu did not change magnetic ordering of Mn atoms. Table 2 shows obtained magnetic parameters for both structures.

As can be seen while analyzing table 2, the total cell magnetization after Cu substitution rises up by 1.35 μB, while difference in (Δ_{tabs} = total - absolute) magnetization drops down. The total magnetization is defined as: $\int(n_{up} - n_{down})\, d^3r$ and the absolute magnetization is $\int Abs(n_{up} - n_{down})\, d^3r$, where n_{up} and n_{down} are magnetic moments coming up from spin up and down respectively.

In order to obtain magnetic moment per atomic site we performed Lowdin charge distribution analysis (LCDA). The LCDA showed, that Mn - d orbital electrons are mostly responsible for magnetization of unit cell, taking over 90% of absolute magnetization value in both cases. The Mn moment is 2.97 μB and 3.02 μB for base and substituted material respectively, in well accordance with [6, 19]. In the first structure (without Cu), magnetic moments located on Ge atoms are small (-0.03μB), similar to the second structure with Cu (-0.05μB). The main difference lies in Fe sites magnetic moments, which in case of Fe_2MnGe are smaller than in Fe_2MnGe:Cu material (all sites average 0.03μB and 0.21μB respectively). Also as can be seen in table 1, distances between Fe-Fe in the case of Cu substituted alloy are similar to those of α-Fe phase, while in pure Fe_2MnGe this distance is shorter. This may be the reason of increase in coupling of iron ions giving a rise in overall magnetization. Also, due to small increase in Ge magnetic moment (coupled antiparallel to Mn) difference in total and absloute magnetization increases, what explains why both absolute and total magnetization (table 2) rises up.

Conclusions

In this paper the influence of Cu substitution in place of Fe atom In Heusler type Fe_2MnGe alloy was studied using density functional theory calculations. The starting structure of Fe_2MnGe was examined in two configurations: non magnetic and ferromagnetic. The Cu atom substitution causes increase in unit cells volume and therefore in distance between magnetic atoms. At the same time it breaks the half metallic character of the minority spin band. A significant increase in magnetization is also observed.

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