The effect of exchange-correlation potentials on magnetic properties of Fe-(Ga, Ge, Al) alloys

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Abstract. This work presents a theoretical study of magnetic properties from first-principles calculations for binary Fe$_{100-x}Z_x$ type alloys ($Z = \text{Ga, Ge, Al}$) in concentration range of $3.125 \leq x \leq 21.875$ at.$\%$. The both, general gradient approximation and local density approximation are considered for the exchange-correlation functional. Ab initio calculations are performed for A2 and D0$_3$ crystal structures. It is shown that for local density approximation, magnetic moments are found in the better agreement with experimental ones. Using the calculated exchange coupling constants for studied compositions, Curie temperatures were estimated by means of mean field approximation. It was found that the obtained Curie temperatures are in qualitative agreement with the experiment.

1. Introduction

The Fe-Ga alloys are successful magnetostrictive materials, which demonstrated two peaks of saturation magnetostriction $\lambda_{001} = 395 \times 10^{-6}$ and $350 \times 10^{-6}$ at room temperature for compositions with $x \approx 19$ at.$\%$ and $x \approx 27$ at.$\%$, respectively [1]. After the discovery of giant magnetostriction in Fe-Ga alloys other Fe-based alloys such as Fe-(Ge, Al) have been investigated in more detail. Each alloy characterizes by increasing magnetostriction with an increase of doping atoms compared with magnetostriction in a pure Fe [2]. According to Ref. [3], in the ab initio calculations of Fe-based alloys, the local density approximation (LDA) in the formulation of Vosko, Wilk and Nusair (VWN) [4] leads to good results for the magnetic properties such as magnetic moments and the exchange parameters $J_{ij}$, while at the same time the general gradient approximation (GGA) in the formulation of Perdew, Burke, and Enzerhof (PBE) [5] in ground state calculations guarantees good agreement of the predicted lattice constant in comparison with the experiment. It is known from the paper by F. Lechermann et al. that commonly used GGA functionals fail to predict for Fe$_3$Al the experimentally stable D0$_3$ structure as the one with the lower total energy [6]. In [7] has shown for Fe$_{100-x}$Ga$_x$, that the LDA-VWN approximation is favored for calculations of the exchange parameters $J_{ij}$. Based on $J_{ij}^{\text{LDA}}$, the Curie temperature obtained using Monte-Carlo simulation was found in better agreement with the experimental data than the $T_C$ obtained using by $J_{ij}^{\text{GGA}}$. Since the accuracy of the LDA and GGA approximations is a very important issue, which in the end determines the reliability of ab initio or first-principles phase stability calculations.
The aim of this paper is a study of magnetic properties of Fe_{100-x}Z_x (Z = Ga, Ge, Al) (3.125 ≤ x ≤ 21.875) alloys within different approximations for the exchange-correlation energy. This article is organized as follows. In Section 2 the details of ab initio calculations are presented. The main results of calculations are discussed in Section 3. Finally, in Section 4, the concluding remarks are presented.

2. Details of ab initio calculations
All calculations were performed using the density functional theory as part of the spin-polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) package [8]. This code is based on the KKR-Green’s function formalism that makes use of the multiple-scattering theory and the electronic structure is expressed in terms of the corresponding Greens function as opposed to Bloch wave functions and eigenvalues. SPR-KKR package has been used for calculations of the Heisenberg’s magnetic exchange coupling parameters (J_{ij}). According to the phase diagrams of Fe-(Ga, Al) systems for considered range, only two phases are experimentally observed [9]. For Fe-Ge system, partially disordered B2 phase appears after x ≈ 12 at.%, whereas for Fe-(Ga, Al) B2 observed in concentration range over x = 25 at.%. To perform the calculations, we used two body-centered cubic A2 (Im3m, #229) and D0_3 (Fm3m, #225) structures. The chemical disorder is treated through coherent potential approximation [8]. In calculations, we used the optimized lattice parameters obtained in our recent works [10, 11, 12] and listed in Table 1. For all SPR-KKR calculations, the exchange-correlation energy was treated by the LDA-VWN [4] and GGA-PBE [5] formulations. For self-consistent cycles (SCF) calculations, 6348 k-points were generated by a k-mesh grid of 45 × 45 × 45. The angular momentum expansion (l_{max}) was restricted to three. All calculations converged to 0.01 mRy of total energy. Magnetic exchange coupling constants were calculated using the spin-polarized scalar-relativistic (SP-SREL) Dirac Hamiltonian with l_{max} = 3 on a k-mesh grid of 57 × 57 × 57 with 4495 k-points.

Table 1. The lattice parameters a_0 (in Å) of A2, and D0_3 structures which used in calculations.

| Alloy | Structure | Concentration x at.% |
|-------|-----------|-----------------------|
|       |           | 3.125     | 6.25      | 9.375     | 12.5      | 15.625     | 18.75     | 21.875     |
| Fe_{100-x}Ga_x | A2 | 2.84 | 2.86 | 2.86 | 2.87 | 2.88 | 2.89 | 2.90 |
|        | D0_3 | 5.69 | 5.71 | 5.73 | 5.74 | 5.75 | 5.76 | 5.76 |
| Fe_{100-x}Ge_x | A2 | 2.84 | 2.85 | 2.86 | 2.87 | 2.88 | 2.89 | 2.90 |
|        | D0_3 | 5.69 | 5.71 | 5.72 | 5.72 | 5.72 | 5.72 | 5.72 |
| Fe_{100-x}Al_x | A2 | 2.84 | 2.85 | 2.86 | 2.87 | 2.87 | 2.88 | 2.88 |
|        | D0_3 | 5.68 | 5.70 | 5.72 | 5.73 | 5.73 | 5.73 | 5.74 |

In order to estimate the Curie temperatures T_C Heisenberg model in the framework of mean field approximation (MFA) has been used [13, 14].

3. Results of ab initio calculations
3.1. Magnetic moments
Let us first discuss the concentration dependences of Fe magnetic moments for Fe_{100-x}Z_x alloys. Magnetic moments as function of Z concentration calculated within LDA-VWN and GGA-PBE potentials are depicted on figure 1.

For A2 phase (see figure 1(a)) we show the partial moments μ_{Fe} and for D0_3 (see figure 1(b)) we show average magnetic moments ⟨μ_{Fe}⟩. For D0_3 phase, in the considered concentration range,
three types of Fe atoms we can distinguish. These are Fe\textsubscript{1} atoms located on 8c Wyckoff position; Fe\textsubscript{2} atoms placed on 4b position and finally Fe\textsubscript{3} atoms, which placed on positions of Z atoms.

As can be seen from the figure in all cases dependencies has identical behavior. Magnetic moments (both partial and average) increases with increasing of Z content up to about \( x \approx 10 \) at.\% and then decreases. The same trends was observed experimentally [15] and theoretically [16, 17]. The magnitudes of magnetic moments are highest for Fe-Ga and lowest for Fe-Al. Meanwhile, for Fe-Ga and Fe-Ge these values are in closest to each other. Obtained results suggest that the magnetic moment values obtained with the help of GGA are about 0.7 \( \mu_B \) beyond than in the case of LDA. Moreover, the values obtained in the LDA approximation are in better agreement with the experimental data [15]. For Fe\textsubscript{78.125}Ge\textsubscript{21.875} alloy with D\textsubscript{0}\textsubscript{3} structure, the obtained \( \mu^{VWN}_x \approx 2.24 \mu_B \) is consistent with experimental data for \( x = 25 \) at.\% (\( \mu^{exp} = 2.17 \mu_B \)) [18].

3.2. Magnetic exchange coupling parameters

The second step of our study is dedicated to magnetic exchange constants calculations. In the figure 2 magnetic exchange parameters depending on the distance between atom pairs are shown. These dependencies are calculated for \( x = 12.5 \) at.\% at their equilibrium lattice parameters.

Magnetic exchange interactions for nearest neighbors (NN) calculated in the case of GGA-PBE are larger in comparison to LDA-VWN case. The differences of between exchange constants calculated by using both functionals (\( J^{VWN}_{ij} - J^{PBE}_{ij} \)) are approximately 4 meV.

In the case of the A2 phase (see figure 2(a)), exchange interaction is about 21 – 25 meV for all alloys and both approximation. The largest values of NN correspond to Fe-Ga (in both LDA-VWN and GGA-PBE cases), while the lowest values correspond Fe-Al.

Figures 2(b-d) show \( J_{ij} \) (d/a) dependencies for D\textsubscript{0}\textsubscript{3} structure of Fe-(Ga, Ge, Al). Since the exchange coupling results from the overlap of electronic wave functions it is obvious that in investigated materials the intersublattice coupling (shorter distance) will be stronger than the intrasublattice one (longer distance). For Fe\textsubscript{87.5}(Ga, Ge)\textsubscript{12.5} the maximum exchange interaction is between Fe\textsubscript{1}-Fe\textsubscript{2,3} (figure 2(b, c)), while for Fe-Al (figure 2(d)) system this maximum is between iron atoms located at the regular positions (Fe\textsubscript{1}-Fe\textsubscript{2}). The intrasublattice interactions are almost twice weaker than intersublattice ones and become close to zero since the third coordination
Figure 2. Exchange coupling constants $J_{ij}$ as a function of distance ($d/a$) between atoms $i$ and $j$ for Fe$_{87.5}$Ga$_{12.5}$ at their equilibrium lattice parameters: (a) A2 structure; (b) Fe$_{87.5}$Ga$_{12.5}$ with D0$_3$ structure; (c) Fe$_{87.5}$Ge$_{12.5}$ with D0$_3$ structure; (d) Fe$_{87.5}$Al$_{12.5}$ with D0$_3$ structure.

shell. In the third coordination shell ($d/a \approx 0.86$) the Fe$_1$-Fe$_1$ exchange parameters split into two contributions ferromagnetic ($\approx 0.2$ meV) and antiferromagnetic ($\approx -3$ meV) interactions. Conceivably this might be connected to the fact, that part of Fe$_1$ atoms are near to iron atoms (Fe$_2$) and the second near Z atoms.

3.3. Curie temperatures

Calculated $J_{ij}$ allowed to obtain the Curie temperatures with the help of MFA. The dependencies of $T_C$ on Z content are shown in figure 3. For all compounds, and both exchange-correlation functionals the dependencies $T_C(x)$ has the same behavior. Curie temperatures have a maximum value at $x = 6.25$ at.% and then decrease with increasing of Z content. $dT_C/dx$ are approximately (except VWN case for Fe-Al) $-24 \div -29$. Curie temperatures calculated using GGA-results of exchange parameters are overestimated in comparison with VWN-results. The difference is approximately 200 K (for $x = 3.125$ at.%) and decreases with increasing Z content to $\approx 120$ K (for $x = 21.875$ at.%). In comparison with the experimental data [19, 20, 21], VWN-MFA yields overestimated values of $T_C$, nevertheless, the qualitative agreement is observed.
Figure 3. The Curie temperature for A2 and D0$_3$ phases of (a) Fe-Ga, (b) Fe-Ge, and (c) Fe-Al as a function of Ga(Ge, Al) concentration. For comparison, the experimental values [19, 20, 21] are given.

4. Conclusion
In this paper, the composition dependence of magnetic properties (such as magnetic moments and magnetic exchange parameters) in Fe$_{100-x}$Z$_x$ ($Z$ = Ga, Ge, Al) ($3.125 \leq x \leq 21.875$) alloys are investigated with the help of first-principles using the SPR-KKR method and different exchange-correlation functionals. Magnetic moments for all considered alloys (both partial and average) increases with increasing of $Z$ content up to about $x \approx 10$ at.\% and then decreases. The magnitudes of magnetic moments are highest for Fe-Ga and lowest for Fe-Al. Obtained results suggest that the magnetic moment values obtained with the help of GGA are about 0.7 $\mu_B$ beyond than in the case of LDA. Investigation of magnetic exchange parameters for Fe$_{87.5}$Z$_{12.5}$ ($Z$ = Ga, Ge, Al) shows that interactions between first neighbors calculated in the case of GGA-PBE are more significant in comparison to LDA-VWN case. In the case of D0$_3$ phase the intrasublattice interactions are two times weaker in comparison with intersublattice ones and become negligible since the third coordination shell. Using exchange interaction constants, the Curie temperatures were estimated with the help of mean field approximation. Curie temperatures calculated using GGA-results of exchange parameters are overestimated in comparison with VWN exchange parameters. It was found that the behavior of obtained Curie temperatures is in qualitative agreement with the experiment. As follows from this investigation
to calculate the magnetic properties of Fe-(Ga, Ge, Al) alloys the local density approximation is more favorable.

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References
[1] Clark A E, Hathaway K B, Wun-Fogle M, Restorff J B, Lograsso T A, Keppens V M, Petculescu G, Taylor R A 2003 *J. Appl. Phys.* **93** 8621
[2] Petculescu G, Wu R, McQueeney R 2012 *Magnetoeelasticity of bcc Fe-Ga Alloys* (Handbook of Magnetic Materials vol 20) ed K H J Buschow (Amsterdam: Elsevier Science B.V.) chapter 3 pp 123-226
[3] Ruban A V, Abrikosov I A 2008 *Rep. Prog. Phys.* **71** 046501
[4] Vosko S H, Wilk L, Nusair M 1980 *Canadian J. of Phys.* **58** 1200
[5] Perdew J P, Burke K, Enzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[6] Lechermann F, Welsch F, Elsässer C, Ederer C, Fähnle M, Sanchez J M, Meyer B 2002 *Phys. Rev. B.* **65** 132104
[7] Matyunina M, Zagrebin M, Sokolovskiy V, Buchelnikov V 2018 *EPJ Web of Conferences* **185** 04013
[8] Ebert H, Ködderitzsch D, Minár J 2011 *Rep. Prog. Phys.* **74** 065101
[9] Kubaschewski O 1982 *Iron-binary phase diagrams* (Berlin: Springer-Verlag)
[10] Matyunina M V, Zagrebin M A, Sokolovskiy V V, Buchelnikov V D 2018 *Materials Research Proceedings* **9** 162
[11] Matyunina M V, Zagrebin M A, Sokolovskiy V V, Buchelnikov V D 2019 *Phase Transit.* **92** 101
[12] Matyunina M V, Zagrebin M A, Sokolovskiy V V, Buchelnikov V D 2019 *B. Russ. Acad. Sci. Ph.* **83** 844
[13] Anderson P W 1963 *Solid State Phys.* **14** 99
[14] Sokolovskiy V V, Buchelnikov V D, Zagrebin M A, Entel P, Sahoo S, Ogura M 2012 *Phys. Rev. B.* **86** 134418
[15] Kawamiya N, Adashi K, Nakamura Y 1972 *J. Phys. Soc. Jpn.* **33** 1318
[16] Khmelevska T, Khmelevskyi S, Mohn P 2008 *J. Appl. Phys.* **103** 073911
[17] Khmelevska T, Khmelevskyi S, Ruban A V, Mohn P 2006 *J. Phys. Condens. Matter* **18** 6677
[18] Adelson E, Austin A 1965 *J. Phys. Chem. Solids* **26** 1795
[19] Arajs S 1965 *Phys. Status Solidi* **11** 121
[20] Ikeda O, Kainuma R, Ohnuma I, Fukamichi K, Ishida K 2002 *J. Alloy. Compd.* **347** 198
[21] Stein F, Palm M 2007 *Int. J. Mat. Res.* **98** 580