**Ab initio** study of DyFe₄Ge₂ alloy

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**Abstract.** Using density functional theory, the magnetic and electronic properties for DyFe₄Ge₂ alloy with four different structures were studied. The exchange-correlation effects were treated by the two approximations: local density approximation (LDA) and LDA+U. It is shown, that for all considered structures both approximations give rise to similar results for magnetic moments and partial densities of states for Fe (Ge) atoms. The DOS calculations for Dy atoms demonstrated significant difference between LDA and LDA+U results. The strongest antiferromagnetic and ferromagnetic interactions were found for iron atoms located on regular sublattices in orthorhombic structures.

1. Introduction

Rare-earth-based intermetallic compounds are interesting due to their strong magnetocaloric, magnetoresistance, magnetostriction, magnetoelastic, and other effects [1, 2, 3]. One of them is the Dy-Fe-Ge ternary system. The X-ray diffraction investigation of this system at 773 K [3] determined 24 single-phase regions, 51 two-phase regions, and 27 three-phase regions. Among them, DyFe₄Ge₂ compound is attractive due to their specific magnetic properties and strong magnetostructural transitions [2]. It is found that DyFe₄Ge₂ at room temperature crystallize with tetragonal ZrFe₄Si₂-type structure, (P₄/2/mnm space group) and at temperature below 55 K the DyFe₄Ge₂ adopts the orthorhombic (Cmmm space group) [1]. The neutron diffraction data has shown the two subsequent magnetic transitions at the temperatures of $T = 45$ K and $T = 28$ K in orthorhombic structure [1]. Liu et al. [2] performed the **ab initio** electronic structure calculations of DyFe₄Ge₂ alloy using the density functional theory in an account of local density approximation including Hubbard parameters. These calculations show that the P₄/2/mnm is stable at high temperatures.

The aim of this work is **ab initio** study of the magnetic properties of the DyFe₄Ge₂ alloy with different structures by using two different approximations.

2. Computation details

The calculations were performed using by Korringa-Kohn-Rostoker Greens function method implemented into the SPR-KKR (A spin-polarized relativistic Korringa-Kohn-Rostoker) package [4]. The exchange-correlation effects were treated by the local density approximation (LDA) in the Vosko-Wilk-Nusair form [5]. In order to better understand the magnetism we also have performed the LDA+U calculations. It should be noted, that $U$ and $J$ are not known for
Dy, so we have employed parameters closer to parameters corresponding to another rare-earth element Gd [6]. The Coulomb repulsion $U$ between localized $f$ and $d$ electrons of Dy atom was set equal to 4.0 eV, and for Fe atom was 1.5 eV. The exchange interaction $J$ for both Dy and Fe atoms was set to 0.5 eV.

To study the electronic and magnetic properties of DyFe$_4$Ge$_2$ alloy, we used the two experimentally established structures, which depicted on Fig. 1: tetragonal $P4_2/mnm$ (No. 136) and orthorhombic $Cmmm$ (No. 65). These structures follow from experimental studies [1] and atoms are locating at the next Wyckoff’s positions: (a) Dy atoms are located at sites $2b$ (0, 0, 0.5), Fe atoms, at sites $8i$ ($x$, $y$, 0), and Ge atoms, at sites $4g$ ($x$, $-x$, 0) ($P4_2/mnm$); (b) Dy$_{1(2)}$ atoms are located at sites $2d$ (0, 0, 0.5) and $2b$ (0.5, 0, 0), Fe$_{1(2)}$ atoms, at sites $8p$ ($x$, $y$, 0) and $8q$ ($x$, $y$, 0.5), and Ge$_{1(2)}$ atoms, at sites $4g$ ($x$, 0, 0) and $4j$ (0, $y$, 0.5) ($Cmmm$).

**Figure 1.** The calculation cells of DyFe$_4$Ge$_2$ alloy with (a) tetragonal ($P4_2/mnm$) and (b) orthorhombic ($Cmmm$) structures

In the present work, the one tetragonal (labeled as #1) and three types of orthorhombic structures (labeled as #2, #3, and #4) were considered. The detailed information about these phases is listed in Table 1. Note that the structural parameters were found from neutron diffraction data at different temperatures [1]. For self-consistent cycles (SCF) calculations, 1320 points were generated by a $k$-mesh grid of $20 \times 20 \times 39$ for the tetragonal system, and 1221 $k$-points were generated by a $k$-mesh grid of $20 \times 20 \times 20$ for the orthorhombic ones. To calculate the exchange coupling constants ($J_{ij}$) and electronic density of states (DOS) for $P4_2/mnm$ phase, $32 \times 32 \times 61$ $k$-mesh grid was created by 4743 number of $k$-vectors. In the case of $Cmmm$ system, the $31 \times 31 \times 31$ $k$-mesh grid was created by 4096 number of $k$-vectors. All calculations converged to 0.01 mRy of total energy. The BROYDEN2 scheme [7] was taken into account to achieve better convergence.

**Table 1.** Structural parameters which obtained experimentally at different temperature for DyFe$_4$Ge$_2$ alloy [1].

| Number of structure | Space group | Temperature | Lattice parameters |
|---------------------|-------------|-------------|--------------------|
|                     |             |             | $a$    | $b$    | $c$    |
| #1                  | $P4_2/mnm$  | 56 K        | 7.2989 | 7.2989 | 3.8609 |
| #2                  | $Cmmm$      | 56 K        | 10.3223| 10.3223| 3.8609 |
| #3                  | $Cmmm$      | 46 K        | 10.3295| 10.3127| 3.8603 |
| #4                  | $Cmmm$      | 40 K        | 10.3307| 10.3138| 3.8537 |
3. Results and discussions
As we mentioned in Section 2, to create the $P4_2/mnm$ and $Cmmm$ structures, we used the experimentally established lattice parameters obtained at the different temperatures (see Table 1). Each of considering structures we named as shown in Table 1, so here and further described they according to these labels.

The calculated energies results of tetragonal and orthorhombic structures using LDA and LDA+$U$ approximations are summarized in Table 2.

Table 2. The calculated energy $E$ (in eV/cell) of considered structures obtained with the LDA and LDA+$U$ approximations.

| Number of structure | Approximation | \#1     | \#2     | \#3     | \#4     |
|---------------------|---------------|---------|---------|---------|---------|
|                     | LDA           | -6300.69| -6300.69| -6304.61| -6304.61|
|                     | LDA+$U$       | -6300.54| -6302.52| -6304.47| -6304.47|

As can be seen, the two exchange-correlation functionals give approximately equal results. From LDA+$U$ calculations, the structure \#2 is more stable at $T = 56$ K in comparison of structure \#1. The same results were obtained in LDA approximation, but the difference is $\approx 10^{-6}$ eV. This is in agreement with experimental data: DyFe$_4$Ge$_2$ undergoes at $T = 55$ K a structural transition $P4_2/mnm \rightarrow Cmmm$ [1].

Figure 2 depicted the calculated magnetic moment per atom Dy/Fe/Ge of DyFe$_4$Ge$_2$ alloy with different structures in an account of LDA and LDA+$U$ approximations.

In general, the magnetic moments $\mu$ of atoms Fe and Ge are change negligible from structure \#1 to \#4. The $\mu_{Fe} \approx 2 \mu_B$ and have the trend of the decrease. In the case of LDA+$U$ approximation, the magnetic moment per atom Dy is $\approx 2 \mu_B$ for structure \#2 (correspond to $Cmmm$ phase). It should be mentioned, the major contribution to the magnetic moment of Dy give the atom located at 2$d$-site (4.2 $\mu_B$) while the atom at 2$b$ position contributes $-0.1 \mu_B$. At the same time for LDA approximation $\mu_{Str.\#2} \approx -0.1 \mu_B$. For structures \#3 and \#4, the
contributions of two different atoms Dy is approximately equal and are \( \approx 4.2 \) (\( \approx 4.5 \)) \( \mu_B \) in an account LDA+U (LDA) approximation.

Figure 3 presents the calculated total density of states of DyFe\(_4\)Ge\(_2\) alloys with the different structures in LDA+U and LDA approximations. For the structure #1, the DOS profiles are similar in the range from \(-6\) to \(2\) eV, and the Fe atoms are determined predominant contribution for both approximations. The range of \(-11 \div -6\) eV is characterized by peaks-band with the predominant contributions by Dy atoms. The LDA calculations show the two peaks at \(\approx -8\) eV (11 sts./eV f.u.), and at \(\approx -7\) eV (1.5 sts./eV f.u.). The LDA+U approximation gives the splitting into several peaks the highest of them are at \(-9.5\) (\(\approx 5\) sts./eV f.u.), \(-9\) (\(\approx 6\) sts./eV f.u.) and \(-8.5\) eV (\(\approx 9\) sts./eV f.u.). The same trend is observed for structure #2, but the height of peaks (see Fig. 3(c)) is the lower than in the Fig. 3(a). As clearly seen in Fig. 3(c)), the significant contribution of Dy atoms is observed in the conduction band (spin-down state) and valence band (spin-up state). This fact can explain the difference in the magnetic moments of Dy between LDA+U and LDA (see Fig. 3(d)) calculations. Figs. 3(i, g) show that the peaks of Dy atoms contribution which appeared in structure #2 in the spin-up state are shifted on the left from the Fermi level and become higher. In insets of Figs. 3(i, g) are depicted the highest of them. Moreover, the split into the two peaks appears at \(\approx -1.6\) eV in the spin-down state for both phases. There are two peaks in the case of LDA calculations (see Figs. 3(f, h)). One of them is in the spin-up state at \(-3.4\) eV and the second is in the conduction band at about \(0.2\) eV. These Dy bands splittings in the spin-up and spin-down density of state are giving rise to Dy magnetic moment of \(\approx 4\) \(\mu_B\).
The magnetic exchange constants $J_{ij}$ were calculated using SCF calculation results within the LDA approximation. The calculated exchange interaction parameters $J_{ij}$ of DyFe$_4$Ge$_2$ alloys as a function of distance $d/a$ between atoms $i$ and $j$ shown Figure 4. The exchange interactions of Ge atoms are insignificant and omitted from the figure. Here and further, the positive exchange constants ($J_{ij} > 0$) presented a ferromagnetic (FM) coupling, whereas the negative ones ($J_{ij} < 0$) indicate an antiferromagnetic (AFM) coupling. The oscillating damped behavior of $J_{ij}$ observed for all structures. We would like to note that this trend is typical for Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange mechanism [10]. The largest FM interactions observed between nearest Fe-Fe atoms located at different sublattices (See Figs. 3(i, g)).

In the case of Str.#1 (which corresponds to $P4_2/mnm$) the AFM interaction (≈ −4 meV) can be found between the nearest neighbor (NN) Fe-Fe. Interaction between NN Fe-Dy is weak FM and is equal approximately to 0.08 meV. Interaction for Fe-Fe in the third coordination sphere becomes FM and achieve ≈ 28 meV. Fourth NN interaction decreases up to zero and oscillates near zero. It indicates the competition behavior between the FM and AFM interactions for this structure. In the case of structures #2–#4 (correspond to $Cmmm$), there are two intrasublattice and five intersublattice interactions. In the case of Str.#2 Fe$_{1(2)}$-Fe$_{1(2)}$ interactions coincide. NN Fe$_{1(2)}$-Fe$_{1(2)}$ interactions in the first coordination shell is AFM (as in the case of Str.#1). Interaction in the second coordination sphere becomes strong FM (≈ 29 meV) and then decreases up to approximately 0 meV. As for intersublattice Fe$_1$-Fe$_2$ this interaction is constant within the four coordination spheres and equal ≈ 7.5 meV. Interactions between Fe and Dy in this

![Figure 4](image-url)
structure are also weak (as for Str.#1). Interaction Fe$_1$-Fe$_1$ for structures #3 (Fig. 4(i)) and #4 (Fig. 4(g)) has the same behavior as for Str.#2 (See Fig. 4(c)). For the first coordination sphere, the magnitude of this interaction is $-12$ meV, at the same time for the second coordination shell is $36$ meV. These values are larger about 1.3 times than for Str.#2. The Fe$_2$-Fe$_2$ has the opposite behavior. This interaction is strong FM ($\approx 40$ meV) in the first coordination shell and is AFM ($\approx -8$ meV) in the second coordination one. Further, these interactions oscillate near $\pm 2$ meV.

The intersublattice interaction Fe$_1$-Fe$_2$ weak depends on distance. Fe-Dy interactions are not so strong as for Fe-Fe ones. Magnetic constants $J_{ij}^{Fe-Dy}$ are larger in #3 and #4 structures. The largest magnitudes are observed for the first neighbors and are $\approx 3$ meV (for Fe$_2$-Dy$_2$) and $\approx -2.5$ meV for Fe$_1$-Dy$_1$. It is interesting to note, that the strongest FM and AFM interactions between Fe$_1$-Fe$_1$ and Fe$_2$-Fe$_2$ nearest atoms correspond to the presence of the largest peaks of Dy atoms contributions in the valence (spin-up) and conductive (spin-down) bands (Figs. 3(f, h) and Figs. 4(f, h)).

4. Conclusion

The electronic and magnetic properties of DyFe$_4$Ge$_2$ with tetragonal and orthorhombic structures from first-principles within the LDA and LDA+$U$ approximations were studied. The ab initio calculations were carried out using the SPR-KKR simulation package. It is shown that results of the magnetic moments per Fe and Ge atoms and the energies of systems weakly depend on approximation choice. The DOS calculations demonstrated closest results within two approximations for Fe (Ge) atoms and a significant difference for Dy ones. The exchange interaction parameters $J_{ij}$ show the strongest antiferromagnetic and ferromagnetic interaction between the iron atoms located on regular sublattice in the first and the second coordination shells for orthorhombic structures, respectively.

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