First-principles study of the structure and properties of Fe-Rh-Ir alloys

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Abstract. The magnetic and structural properties of FeRh₁₋ₓIrₓ (x = 0.125, 0.25, 0.375, and 0.5) alloys were studied using ab initio calculations. The two structure types (CuAu and CsCl) were considered. The equilibrium lattice parameters, total energy and magnetic moments as well as total and partial densities of states for Fe-Rh-Ir with different magnetic ordering were obtained. It is shown that the CuAu-type structure with AF-III configuration is energetically favourable for all compositions under study. The spin polarization at the Fermi level for FeRh₀.₁₂₅Ir₀.₈₇₅ ordered ferromagnetically is found to be 85 %.

1. Introduction

Fe-Rh compounds are among the most heavily investigated systems due to the possibility of their practical application in magnetic recording, magnetic cooling, and spintronics devices [1-4]. The most interesting compositions are equiatomic or near-equiatomic ones (Fe₉₀Rh₁₀ and Fe₅₁Rh₄₉), which crystallize to the CsCl-type structure. They reveal a metamagnetic phase transition between antiferromagnetic (AFM) and ferromagnetic (FM) phase in the vicinity of room temperatures. Moreover, the metamagnetic transition accompanies by about of 1 % change in the cell volume [5]. As a consequence, the large change in magnetization, the giant magnetoresistance [5], and magnetocaloric effect [6, 7] have been observed. For instance, according to Ref. [5] the change in the resistivity dR/R was approximately 50% upon magnetic field change of 15 T. In regard to magnetocaloric properties of Fe₅₁Rh₄₉ alloy [7], the adiabatic temperature change was ≈ 13 K at a temperature of 310 K and magnetic field changes from 0 up to 2 T.

Generally, the magnetic order as well as magnetic and magnetocaloric properties of Fe-Rh alloys depends strongly on the dopant concentration. Therefore, it is important to study the doping effect of 3d transition metal elements in a parent compound with an aim to analyze its ground state properties. For instance, the effect of iridium addition to Fe-Rh alloys was discussed in Ref. [8]. The authors studied a series of compositions such as Fe₄₉.₅Rh₁₅.₅Ir₁₋ₓ (c = 1.5, 3.0, 5.₀, 6.₅), Fe₄₉₀.₅Rh₁₅.₀, and Fe₄₂Rh₄₈ alloys. It was shown that the Ir-doped compounds have an AFM order. The properties of FeRhₓ₋₄ₓM₄ₓ alloys (M=Fe, Co, Ni, Pd, Ir and Pt) have been studied in Ref. [9]. The authors presented also a magnetic phase diagram for FeRh₁₋ₓIrₓ (x = 0-0.2) and have shown that a first-order AFM-paramagnetic (PM) transition accompanies by a volume expansion. Goto et. al. [10] reported the...
magnetic properties of FePt$_{1-x}$Ir$_x$ ($0 \leq x \leq 0.6$) thin films, which have the CuAu-type structure. They have found that the Ir substitution destroys ferromagnetism, and for compositions with $x > 0.35$, the alloys become antiferromagnetically ordered.

Theoretical studies help to describe and understand the phenomena occurring in the material. In works [11, 12], Fe-Rh-Z ($Z=$Mn, Pd, Ni) alloys were investigated using first-principle methods. It has been shown that the addition of third element into Fe-Rh system slightly changes the optimized lattice parameter and stimulates the martensitic phase transformation. The properties of ordered FeRh, FePd, MnRh and MnPd alloys were theoretically studied in Ref. [13]. The authors discussed total energies for studied alloys with CsCl-type and CuAu type structures.

Our work is devoted to theoretical studies of the structure and magnetic properties of FeRh$_{1-x}$Ir$_x$ alloys ($x = 0.125, 0.25, 0.375, 0.5$) by first-principle methods.

2. **Computational details**

The structural and magnetic properties of Ir-doped Fe-Rh alloys are investigated using the density functional theory which implemented in the Vienna Ab Initio Simulation Package (VASP) [14]. Calculations were carried out within the generalized gradients approximation (GGA) in the Perdew, Burke, and Ernzerhof (PBE) formulation. Computations were fulfilled for two supercells (CuAu- and CsCl-type) containing 16 atoms with different initial spin configurations (nonmagnetic (NM), FM and AFM). For CuAu-type structure, NM, FM, AFM-I, AFM-II, and AFM-III configurations were assumed (See, Figure 1).

![Figure 1. Magnetic spin configurations for CuAu-type ordered structure (a) FM, (b) AFM-I, (c) AFM-II, (d) AFM-III.](image)

While in the case of CsCl-type structure, NM, FM, and AFM spin ordering were taking into consideration (See, Figure 2). For both structures, the rhodium and palladium atoms have a small magnetic moment (less than 1 $\mu_B$).

![Figure 2. Magnetic spin configurations for CsCl-type ordered structure (a) FM, (b) AFM.](image)
The PAW potentials (projector augmented wave) of Fe (3d$_7^7$, 4s$^1$), Rh (4d$_8^8$, 5s$^1$), Ir (5d$_8^8$, 6s$^1$) were taken from the standard VASP database. The first Brillouin zone was divided into $12 \times 12 \times 12$ k-points using the Monkhorst–Pack scheme. The cutoff energy of 400 eV was used. Gaussian smearing type was taking for Fermi surface smearing (width of $\sigma = 0.2$ eV).

3. Results of calculations
The lattice parameters, total energy and magnetic moments for FeRh$_{1-x}$Ir$_x$ alloys ($x = 0.125$, 0.25, 0.375, and 0.5) with different magnetic ordering are presented in Table 1-4.

![Figure 3. Two different unit cells (fct and bct) for the CuAu-type ordered structure.](image)

Table 1. The calculated lattice parameters, energy, total magnetic moments for FeRh$_{0.875}$Ir$_{0.125}$ with different magnetic ordering. The favour magnetic order is marked by bold font.

|                  | Lattice param. (in Å), $a$ | Lattice param. (in Å), $c$ | Total magn. mom. ($\mu_B$/f.u.), $M_{tot}$ | $E$ (eV/cell)          |
|------------------|---------------------------|---------------------------|--------------------------------------------|------------------------|
| **CsCl-type**    |                           |                           |                                            |                        |
| FM               | 3.006                     | 4.192                     | -126.067                                   |                        |
| AF               | 2.989                     | 0                         | -126.728                                   |                        |
| NM               | 2.924                     | -                         | -118.579                                   |                        |
| **CuAu-type**    |                           |                           |                                            |                        |
| FM               | 3.780                     | 3.628                     | 2.572                                      | -125.799               |
| AF-I             | 3.791                     | 3.626                     | 0                                          | -126.294               |
| AF-II            | 3.875                     | 3.513                     | 0                                          | -125.999               |
| **AF-III**       | 3.898                     | 3.463                     | 0                                          | **-126.843**           |
| NM               | 3.687                     | 3.602                     | -                                          | -123.977               |

From the data obtained it can be concluded that the AFM-III phase of CuAu-type structure is energetically favourable for all compositions under study. It is seen from the tables that the equilibrium lattice parameter changes with increasing Ir concentration. The lattice parameters $a$ for an energetically favorable configuration ($a = 3.898$, 3.895, 3.883, 3.875 for FeRh$_{1-x}$Ir$_x$ ($x = 0.125$, 0.25, 0.375, 0.5), respectively) decrease with increasing iridium content, and the lattice parameters $c$ ($c=3.463$, 3.470, 3.492, 3.508 for $x= 0.125$, 0.25, 0.375, 0.5, respectively) increase with increasing iridium content.
Table 2. The calculated lattice parameters, energy, total magnetic moments for FeRh\textsubscript{0.75}Ir\textsubscript{0.25} with different magnetic ordering. The favour magnetic order is marked by bold font.

| Lattice param. (in Å), a | Lattice param. (in Å), c | Total magn. mom. (\(\mu_0\)/f.u.), \(M_{tot}\) | \(E\) (eV/cell) |
|-------------------------|-------------------------|---------------------------------|----------------|
| CsCl-type               |                         |                                 |                |
| FM                      | 3.007                   | 4.182                           | -127.523       |
| AF                      | 2.990                   | 0                               | -128.301       |
| NM                      | 3.092                   | -                              | -121.453       |
| CuAu-type               |                         |                                 |                |
| FM                      | 3.780                   | 3.628                           | -127.448       |
| AF-I                    | 3.797                   | 3.623                           | 0              | -127.935       |
| AF-II                   | 3.866                   | 3.521                           | 0              | -127.599       |
| AF-III                  | 3.895                   | 3.470                           | 0              | -128.495       |
| NM                      | 3.693                   | 3.600                           | -              | -125.794       |

Table 3. The calculated lattice parameters, energy, total magnetic moments for FeRh\textsubscript{0.625}Ir\textsubscript{0.375} with different magnetic ordering. The favour magnetic order is marked by bold font.

| Lattice param. (in Å), a | Lattice param. (in Å), c | Total magn. mom. (\(\mu_0\)/f.u.), \(M_{tot}\) | \(E\) (eV/cell) |
|-------------------------|-------------------------|---------------------------------|----------------|
| CsCl-type               |                         |                                 |                |
| FM                      | 3.009                   | 4.179                           | -128.893       |
| AF                      | 2.991                   | 0                               | -129.871       |
| NM                      | 3.028                   | -                              | -122.055       |
| CuAu-type               |                         |                                 |                |
| FM                      | 3.777                   | 3.633                           | -129.117       |
| AF-I                    | 3.795                   | 3.628                           | 0              | -129.566       |
| AF-II                   | 3.858                   | 3.528                           | 0              | -129.225       |
| AF-III                  | 3.883                   | 3.492                           | 0              | -130.140       |
| NM                      | 3.697                   | 3.601                           | -              | -127.615       |

Table 4. The calculated lattice parameters, energy, total magnetic moments for FeRh\textsubscript{0.5}Ir\textsubscript{0.5} with different magnetic ordering. The favour magnetic order is marked by bold font.

| Lattice param. (in Å), a | Lattice param. (in Å), c | Total magn. mom. (\(\mu_0\)/f.u.), \(M_{tot}\) | \(E\) (eV/cell) |
|-------------------------|-------------------------|---------------------------------|----------------|
| CsCl-type               |                         |                                 |                |
| FM                      | 3.010                   | 4.170                           | -130.291       |
| AF                      | 2.992                   | 0                               | -131.439       |
| NM                      | 2.929                   | 0                               | -123.805       |
| CuAu-type               |                         |                                 |                |
| FM                      | 3.777                   | 3.634                           | -130.757       |
| AF-I                    | 3.796                   | 3.627                           | 0              | -131.191       |
| AF-II                   | 3.851                   | 3.533                           | 0              | -130.847       |
| AF-III                  | 3.875                   | 3.508                           | 0              | -131.777       |
| NM                      | 3.702                   | 3.600                           | -              | -129.415       |
The partial magnetic moment of Fe ($M_{Fe}$, $\mu_B$) for an energetically favourable structure (AFM-III) is found to be $\pm 2.850$, $\pm 2.821$, $\pm 2.781$, and $\pm 2.749$ for FeRh$_{0.875}$Ir$_{0.125}$, FeRh$_{0.75}$Ir$_{0.25}$, FeRh$_{0.625}$Ir$_{0.375}$ and FeRh$_{0.5}$Ir$_{0.5}$, respectively. As can be seen from the presented data, the magnetic moment on the iron atom decreases with increasing Ir content. In the case of antiferromagnetic (AF-III) in CuAu-type cell, the magnetic moments of iridium and rhodium atoms are equal to zero.

Furthermore, in order to determine the phase stability of FeRh$_{0.875}$Ir$_{0.125}$, FeRh$_{0.75}$Ir$_{0.25}$, FeRh$_{0.625}$Ir$_{0.375}$, FeRh$_{0.5}$Ir$_{0.5}$ alloys, we calculate the formation energy as difference between the total energy and partial total energies of the pure elements in their equilibrium bulk structures. Figure 4 shows the formation energies for all compositions under study. We can see that the total energy of each Fe-Rh-Ir composition is lower than the sum of total energies of pure elements. Hence we can suggest that these compounds should be stable at equilibrium conditions.

![Figure 4. Formation energies for the FeRh$_{0.875}$Ir$_{0.125}$, FeRh$_{0.75}$Ir$_{0.25}$, FeRh$_{0.625}$Ir$_{0.375}$, FeRh$_{0.5}$Ir$_{0.5}$ alloys.](image)

Additionally, we calculate the total and partial densities of states for the Fe-Rh-Ir alloys with high temperature ferromagnetic phase (CsCl-type). We estimate also the spin polarization as follows: $P = (N^\uparrow(E_F) - N^\downarrow(E_F))/(N^\uparrow(E_F) + N^\downarrow(E_F))$, where $N^\uparrow(E_F)$ and $N^\downarrow(E_F)$ are the electron density states at the Fermi level ($E_F$) for the spin direction up and down, respectively.

![Figure 5. The total density of electronic states for the FeRh$_{0.5}$Ir$_{0.5}$ alloys (a) and the projected density of states for t$_{2g}$ and e$_g$ orbitals (b). Zero energy indicates the position of the Fermi level.](image)
Figure 6. The total density of electronic states for the FeRh$_{0.5}$Ir$_{0.5}$ alloys and the projected density of states for t$_{2g}$ and e$_g$ orbitals.

Figures 5 and 6 illustrate the total and d-orbital resolved (t$_{2g}$ and e$_g$) densities of states for FeRh$_{0.125}$Ir$_{0.875}$ and FeRh$_{0.5}$Ir$_{0.5}$ alloys, respectively. We find that for FeRh$_{0.125}$Ir$_{0.875}$, the spin polarization is approximately 85%, while for FeRh$_{0.5}$Ir$_{0.5}$, it is equal to 76%. As can be also seen from these figures, the main contribution to the density of states near the Fermi level follows from t$_{2g}$ state electrons. Hence, they give the main contribution to the spin polarization of these compounds.

4. Conclusion

In summary, in our work we studied structural and magnetic properties for two types of crystalline structures (CuAu-type and CsCl-type). From the data obtained it can be concluded that the AFM-III phase of CuAu-type structure is energetically favourable for FeRh$_{1-x}$Ir$_x$ ($x = 0.125, 0.25, 0.375, and 0.5$). The spin polarization for the high temperature ferromagnetic phase FeRh$_{0.125}$Ir$_{0.875}$ alloy is approximately 85%.

Acknowledgments

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