Updating the calculation of the concentration dependence of full energy and formation energy of sigma-phase of the Fe-V system for the basic state

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Abstract. The purpose of this work is to study the region of existence of the sigma phase of the Fe-V system. Since this phase is stable up to low temperatures, up to temperature of the ground state, at which quantum-mechanical calculations are carried out. This one allows testing quantum-mechanical calculations for sigma – phase Fe-V alloys. The original algorithm for calculating the minimum total energy was developed and tested depending on two independent variables [1, 2, 3]. The optimized values of the lattice parameters for the σ-phase alloys of the Fe-V system are calculated. Dependence of the mixing energy of the σ – phase as a function of the composition x (V) of the sigma - phase of the Fe-V system was obtained. The calculations were carried out using the license package of quantum-mechanical calculations WIEN2k.

1. Introduction
In previous works [2–4], optimized values of the crystal lattice parameters and the formation energy of stoichiometric consist for the Fe – V system with the sigma phase structure was calculated. Stable energy configurations were chosen for various (Fe-40% V, Fe-60% V) of stoichiometric compositions of chemical compounds. However, a large drawback of the previously performed calculations was the different values of the initial calculation conditions (Rm radius “cores” and the number of attached plane waves kmax), as well as the absence of allowance for the relaxation of the crystal lattice filled with atoms of components whose size factor was approximately 5% (15%) in linear size (or atomic volumes), respectively. In the present work, the previously developed calculation algorithm is used to more accurately calculate the energy of formation of the sigma phase for stoichiometric alloys in the Fe-V system. It was carried out: 1) the use of the same initial conditions (external structural parameters according to the terminology of [5]) calculation, both for pure components and chemical compounds of all stoichiometric compositions; and also 2) taking into account the relaxation of atoms (carrying out optimization according to the internal powers of freedom) inside the crystal lattice of a chemical compound with a sigma phase structure.

2. Assessment of lattice parameters σ – phases of pure components
According to with the developed methodology [1–3], the initial values of the crystal lattice parameters of metastable σ – phases of pure components (a(Fe), c(Fe) and {a(V), c(V)}) were obtained from the approximation of the equality of the occupied volume per atom for both Fe and V in the σ and BCC phases, respectively [2–3].
In this work, we used the radius of muffin-tin in the σ phases for core of Fe is 2.03 a. e. and for cores of V is 2.10 a. e. The total energy was minimized according to [1.3]. First, they were minimized by the parameter “a” under the condition c = const, then by c under the condition a = const. This procedure was repeated until the minimum energy values calculated in different directions were equal (δE = 10⁻⁷ Ry / cell was chosen as the criterion for exiting the cycle as agreed). Thus, the optimized values of the lattice parameters (a, c) and energy were calculated for paramagnetic (PM) V and ferromagnetic (FM) Fe (table 1).

**Table 1.** The calculated values of the total energy and optimized lattice parameters of the σ phases of the pure components of FM Fe and PM V.

|       | E, Ry/cell   | a, Bohr     | c, Bohr     |
|-------|--------------|-------------|-------------|
| Fe    | -76368.0380325 | 16.55552    | 8.653538    |
| V     | -56959.26356851 | 17.51851    | 9.020975    |

3. Calculation of the equilibrium lattice parameters for σ-phase alloys of the Fe-V system

In order to assess the equilibrium lattice parameters for σ – phase alloys of the Fe – V system, we used the data presented in table 1 and the Vegard rule for the lattice parameters of the σ – phase depending on the composition, similar to [4]. Thus, the initial (seed) values of the lattice parameters were obtained for different stoichiometric compositions of the σ-phase for different configurations in order to find the minimum total binding energy of the σ-phase (see table 2 Fe-33% V, Fe-40% V, Fe-60% V) in space (a, c) for stoichiometric alloys of chemical compounds of the Fe-V system.

**Table 2.** Initial (starting) values of the lattice parameters for σ-phase alloys of the Fe-V system.

| Configuration | atom %V | a, Bohr     | c, Bohr     |
|---------------|---------|-------------|-------------|
| V⁰ Fe¹²V⁶ Fe¹⁴Fe⁰⁸Fe¹⁴ (AC) | 30      | 16.844417   | 8.7637691   |
| Fe²⁰V⁰⁴Fe¹⁴Fe⁰⁸V⁰⁸ (BE) | 40      | 16.940716   | 8.8005128   |
| V²⁰Fe⁰⁸V⁰⁸Fe³²V⁰⁸ (BD) | 60      | 17.133314   | 8.8740002   |

4. Conclusion

To obtain optimized lattice parameters, the total energy was minimized by coordinates (a and c) described for pure components. (the criterion for exiting the cycle, as agreed, was selected by energy δE = δE=10⁻⁷ Ry / cell and optimization criteria by force δF = 0.5 mRy / Bohr). Input values are calculation parameters in table 3. Thus, optimized values of the lattice parameters and formation energy for alloys were obtained. (see table 3 Fe-33%V, Fe-40%V, Fe-60%V).

**Table 3.** Input values of calculation parameters for chemical compounds with the structure of the σ-phase of stoichiometric compositions.

| Alloy composition | Rm(V), Bohr | Rm(Fe), Bohr | Kmax | Force, mRy/Bohr |
|-------------------|-------------|--------------|------|----------------|
| Fe                | ---         | 2.03         | 2000 | 0.5            |
| Fe-33%V           | 2.12        | 2.03         | 2000 | 0.5            |
| Fe-40%V           | 2.12        | 2.03         | 2000 | 0.5            |
| Fe-60%V           | 2.12        | ---          | 2000 | 0.5            |
| V                 | 2.12        | 2.03         | 2000 | 0.5            |

Optimization calculations of the energy of formation of alloys with the structure of the sigma phase of the Fe-V system were obtained from the data in table 3 (table 4). From a comparison of the results of the present work and those carried out earlier [4], it follows that when the input calculation conditions
change (radius $R_m$ “cores”, $K_{\text{max}}$ increases, the number of attached plane waves and allowance for lattice relaxation) see table. 4, the energy of formation of alloys with the structure of the sigma phase of the Fe-V system decreases. For Fe-40% V alloy at 0.23929 Ry / cell and for Fe-40% V at 0.56797 Ry / cell see table. 4. Thus, we can talk about increasing the accuracy of minimization calculating the formation energy in comparison with the calculation results presented in [4]. As an illustration of the calculation results carried out in this work, the graphs of the total energy (Ry / Cell) $\sigma$ – phases of Fe – 40% V alloys (figure 1) and Fe – 60% V alloys (figure 2) dependence on volume, calculated at variations in “c” with $a = \text{const}$ — triangles and variations in a (c = const) – circles for the ground state in units (Ry / cell). According to the results of table. 4, a graph of the dependence of the mixing energy of the $\sigma$-phase relative to the $\sigma$-phases of pure components as a function of the composition $x$ (V) of the sigma-phase of the Fe-V system was calculated (figure 3).

Table 4. The results of calculations of the lattice parameters, the total energy and the mixing energy of chemical compounds of stoichiometric compositions with the structure of the sigma phase of the Fe-V system relative to the sigma phases of pure components ($dE_{\text{mix}}$).

| Alloy  | $x$, %(V) | $a$, (bohr) | $c$, (bohr) | $E$, Ry/cell | $dE_{\text{mix}}$, Kj/mol |
|--------|-----------|-------------|-------------|--------------|----------------------------|
| Fe     | 0         | 16.5555240  | 8.65353829  | -76368.03381 | 0                          |
| Fe-30% V | 0.3       | 16.5769989  | 8.61712595  | -69898.81810 | 0.5366                     |
| Fe-40% V | 0.4       | 16.5765821  | 8.69679130  | -68604.93196 | 0.5926                     |
| Fe-60% V | 0.6       | 16.8396677  | 8.72393356  | -64723.15788 | 0.5633                     |
| V      | 1         | 17.5185127  | 9.02097479  | -56959.26357 | 0                          |

Table 5. Comparison of the obtained calculation results and those obtained earlier [4].

| Alloy  | $x$, %(V) | $E_1$, Ry/cell [3] | $E_2$, Ry/cell | $\text{abs}(E_2-E_1)$, (Ry/cell)/(Kj/моль) |
|--------|-----------|-------------------|--------------|---------------------------------|
| Fe-40% V | 0.4       | -68604.69267      | -68604.93196 | 0.23929/10.47                   |
| Fe-60% V | 0.6       | -64722.58991      | -64723.15788 | 0.56797/24.85                   |

Figure 1. The total energy (Ry/cell) as a function of volume in different coordinates for the $\sigma$ phase alloy 40%$(V)\text{Fe}_{12}V_{15}\text{Fe}_{14}\text{Fe}_{8}\text{V}_{8}\text{Fe}_{14}$, calculated for $RmFe=2.03$, $RmV=2.10$ for variation for c for $a=\text{const}$ – triangles and for variation for a for $c=\text{const}$ – circles.
Figure 2. The total energy (Ry/cell) as a function of volume in different coordinates for the σ phase alloy 60\%(V) V_{12}Fe_{14}V_{8}Fe_{8}V_{8}, calculated for RmFe=2.03, RmV=2.10 for variation for c for a=const – triangles and for variation for a for c=const - circles.

Figure 3. The dependence of the mixing energy of the σ phase on the composition of X\_v relative to the σ phases of the pure components of the Fe - V system for the ground state (Ry / cell).
5. Conclusion
It should be noted that the calculations for all alloys of the Fe – V system were performed under the same calculation conditions (table 3). In the future, it is planned to carry out calculations of alloys of other stoichiometric compositions and choose stable configurations for the Fe-V system to more accurately plot the sigma phase formation energy curve, depending on the composition.

Acknowledgments
The studies were carried out with the financial support of the RFBR Fund in the framework of a scientific project no. 19-03-00530.

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