Quantum-mechanical calculations of the concentration dependence of the total energy of sigma-phase of the Fe-V system for the ground 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. The original algorithm for finding the minimum total energy was developed and tested depending on two independent variables. 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
Alloys with the bcc structure of the Fe – Cr (V) system are the basis of ferritic steels and are of interest as materials for the claddings of fuel elements for fast neutron reactors. Ferritic steels have higher radiation stability in reactor conditions compared with austenitic steels at a temperature of 600-700°C. It is known that the sigma phase in the Fe-Cr system is stable at temperatures above 450°C. Whereas in the Fe-V system the sigma-phase is stable starting from the ground state up to 1320°C. Therefore, from a methodological point of view, it is logical to carry out quantum-mechanical calculations for the ground state starting from the Fe – V system rather than the Fe – Cr system, due to the stability of the sigma phase at elevated temperatures. Thus, for the Fe - V system, it is possible to compare the calculated the enthalpy of formation for the ground state by comparing it with the experimental stable state for solutions based on the sigma phase in accordance with the experimental phase diagram. Whereas for solutions based on a sigma phase in the Fe-Cr system, it is required, firstly, to calculate the enthalpy of formation of this phase for the ground state, and secondly, to additionally carry out calculations for the excess entropy depending on the composition, taking into account both configurational and vibrational (at least in the harmonic approximation), electronic and magnetic contributions to the excess Gibbs energy.

For this reason, alloys of the Fe - V system became the object of quantum mechanical and semiempirical calculations. The aim of this work is to study the region of existence of the σ phase of the Fe – V system for the ground state.

2. The calculation method
Sigma – phase (σ) has tetragonal symmetry (136_P42/mnm_) of the chemical compound Fe_{0.5x}V_{0.5y}, containing 30 atoms in the cell of the crystal lattice. Thus, the task of minimizing the total energy is to
find the minimum energy in the space of 2 independent lattice parameters (a and c) for which the method of searching for the minimum total energy using the Murnaghan equation in the WIEN2k package is incorrect. The authors developed and tested the original algorithm for finding the minimum total energy depending on two independent variables (crystal lattice parameters) [1]. First, we checked the convergence of the procedure finding the total energy depending on the number of iterations - Figs. 1 and 2.

2.1. Assessment of the lattice parameters σ - phases of pure components

In accordance with the developed methodology [1-2], the lattice parameters of the metastable σ – phases of the pure components (αFe, σFe) and (αV, σV) were estimated from the approximation of the equality of the volumes by atom of Fe and V in s and BCC phases.

The muffin-tin radii were used in s - phases of 1.91 a.e. for Fe and 2.0 a.e. for V, respectively. The total energy was minimized for different “coordinates”: for the parameter “a” under the condition h = c / a = const, then for the parameter h under the condition a = const, this procedure was repeated until the minimum energy values calculated in different directions coincided (exit criterion from the cycle, as agreed, 10^{-7} Ry/cell was selected). To verify convergence, we obtained graphs of the total energy of pure iron in the s phase in the ferromagnetic state (see Fig. 1.2). From Fig. 1.2 it follows that the proposed algorithm converges starting from the 15th iteration. Thus, the optimized lattice parameters (a, c) and energy were calculated for paramagnetic (PM) V and ferromagnetic (FM) Fe (see Table 1, Fig. 3.4).

|     | E, Ry/cell | a, Bohr | c, Bohr | c/a     |
|-----|-----------|---------|---------|---------|
| Fe  | -76367.269541 | 16.3786767 | 8.665802 | 0.52909047 |
| V   | -56958.82024375 | 17.4896492 | 9.0512075 | 0.51751796 |

**Table 1.** The calculated energies and lattice parameters of σ-phases of pure FM Fe and PM V.

**Figure 1.** The total energy (Ry / cell) of the Sigma – phase of Fe as a function of the number of iterations (N) with variation along “a” with c / a = 0.52909 = const
2.2. Assessment of the lattice parameters for alloys $\sigma$–phase of pure components Fe-V

To calculate the equilibrium lattice parameters for $\sigma$-phase alloys of the Fe-V system, we used the data presented in Table 1 and the Vegard rule for $s$-phase crystal lattice parameters depending on the composition. Thus, the initial values of the lattice parameters were obtained for different compositions of the $\sigma$-phase in order to find the minimum total binding energy of the $\sigma$-phase of alloys of 60 at. % V and 40 at. % V in the space (a, c) for alloys of the Fe-V system - table 2.

Table 2. Initial (starting) values of the lattice parameters for $\sigma$–phase alloys of the Fe-V system

| Configuration | a, %V | a, bohr$^3$ | c, bohr | $\eta$ |
|---------------|-------|-------------|---------|--------|
| Fe$_2$V$_4$Fe$_8$V$_8$ (BE) | 40 | 16.8230657 | 8.8199641 | 0.5242780 |
| V$_2$Fe$_4$V$_8$Fe$_8$V$_8$ (BD) | 60 | 17.0452602 | 8.8970452 | 0.5219660 |

2.3. Optimization calculations of the crystal lattice parameters of $\sigma$–phase the Fe-V system

To obtain optimized lattice parameters, the total energy was minimized for different “coordinates”: for the parameter “a” under the condition c/a = const, then for the parameter c/a under the condition a = const, this procedure was repeated until the minimum energy values calculated in different directions coincided (criterion for exiting the cycle, as agreed, selected 10$^{-7}$ Ry / cell). Thus, the optimized values of the lattice parameters (a, c) and the energy of $\sigma$-phases of ferromagnetic alloys were calculated (Table 3).

Table 3. The optimized lattice parameters for $\sigma$–phase alloys of the Fe-V system

| Configuration | a, %V | a, bohr$^3$ | c, bohr | $\eta$ |
|---------------|-------|-------------|---------|--------|
| Fe$_2$V$_4$Fe$_8$V$_8$ (BE) | 40 | 16.5637751 | 8.7025976 | 0.5253994 |
| V$_2$Fe$_4$V$_8$Fe$_8$V$_8$ (BD) | 60 | 16.8291364 | 8.7512950 | 0.5200086 |

3. Results of calculations

Minimization of the total energy in the space of the lattice parameters of the s-phase made it possible to obtain equilibrium values of the s-phase energy of the alloys of various configurations of the Fe-V system (see table 4).

Analyzing table 4, we can conclude that for an alloy with a composition of 40% (V) the equilibrium configuration is Fe$_2$V$_4$Fe$_8$V$_8$ (BE-abbreviated spelling of the types of sub-lattices filled with vanadium atoms), for an alloy with a composition of 60% (V) the equilibrium configuration is V$_2$Fe$_4$V$_8$Fe$_8$V$_8$ (BD). As an illustration of the choice were obtained the total energy (Ry/cell) as
a function of volume for all configurations (see table 4) for the σ phase alloy with a composition of 40% (V) (see fig. 3,4,5), calculated for $R_{m\text{Fe}}=2.13$, $R_{m\text{V}}=1.94$ for variation for $c/a$ for $a=\text{const}$ and for variation for a for $c/a=\text{const}$. The energy (Ry / cell) of the Sigma phase of the 40% (V) alloy was obtained for various distributions of Fe and V atoms over 5 sublattices depending on the volume for variation for “a” (for $c/a = \text{const}$) for the configurations ($\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ ) (BC), ($\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$) (BD), ($\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$) (BE) (see table 5, figure 6) and for variation for “c/a” (for $a = \text{const}$) for the configurations ($\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ ) (BC), ($\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$) (BD), ($\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$) (BE) (see table 4, figure 7).

**Table 4.** The optimized values of energy $\sigma$–phases of alloys of various configurations of the Fe-V system

| Configuration | at. % V | $V,$ bohr$^3$ | E, Ry/Cell |
|---------------|---------|---------------|------------|
| $\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ (BC) | 40 | 2353.592216 | -68604.44413255 |
| $\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ (BD) | 40 | 2430.381166 | -68604.36745681 |
| $\text{Fe}_{12}\text{V}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ (BE) | 40 | 2387.632891 | -68604.69266858 |
| $\text{V}_{12}\text{Fe}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ (BC) | 60 | 2507.265783 | -64722.25261074 |
| $\text{V}_{12}\text{Fe}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ (BD) | 60 | 2478.540300 | -64722.58991302 |
| $\text{V}_{12}\text{Fe}_{4}\text{V}_{8}\text{Fe}_{8}\text{Fe}_{12}\text{V}_{4}$ (BE) | 60 | 2537.779471 | -64722.23080655 |

Thus, for a 40% (V) alloy, it is energetically efficient to fill the C and D sub-lattices with Fe atoms and an E sub-lattice. For an 60% (V) alloy, it is energetically beneficial to fill the C and E sub-lattices with V atoms and the D sub-lattice with Fe atom (see Table 4). Table 3 shows the equilibrium lattice parameters for $\sigma$–phase alloys of the Fe-V system. The lattice parameters “a” and “c” as a function of the composition Xv of the sigma phase of the Fe-V. The lattice parameters “a” and “c” as a function of the composition Xv of the $\sigma$–phase of the Fe-V was obtained (see fig.8). From tables 3, 4 (Fig. 8) it follows that with increasing $X_v$, the parameters (“a”, “c”) and the unit cell volume increase. The deviation of the lattice parameters from the Vegard rule of the alloy (40% V) for parameters “a” and “c” is 1.57% and 1.35%, respectively. Similarly, for the alloy (60% V) for these values, respectively, are 1.28% and 1.67% (see Fig. 8), which is explained by the difference in the sizes of the Fe and V. According to the results of the table 4, was plotted the dependence of the mixing energy of the $\sigma$–phase on the composition x (V) of the $\sigma$–phase of the Fe – V system (Fig. 9).
**Figure 3.** The total energy (Ry/cell) as a function of volume in different coordinates for the σ phase alloy 40\% (V) \((\text{Fe}_{2}^{12}\text{V}_{4}^{12}\text{Fe}_{8}^{14}\text{Fe}_{8}^{14}\text{V}_{8}^{14}\text{Fe}_{8}^{14})\), calculated for \(R_{m}\text{Fe}=2.13, R_{m}\text{V}=1.94\) for variation for \(c/a\) for \(a=\text{const}\) – triangles and for variation for \(a\) for \(c/a=\text{const}\) - circles.

**Figure 4.** The total energy (Ry/cell) as a function of volume in different coordinates for the σ phase alloy 40\% (V) \((\text{Fe}_{2}^{12}\text{V}_{4}^{12}\text{Fe}_{8}^{14}\text{Fe}_{8}^{14}\text{V}_{8}^{14}\text{Fe}_{8}^{14})\), calculated for \(R_{m}\text{Fe}=2.13, R_{m}\text{V}=1.94\) for variation for \(c/a\) for \(a=\text{const}\) – triangles and for variation for \(a\) for \(c/a=\text{const}\) - circles.

**Figure 5.** The total energy (Ry/cell) as a function of volume in different coordinates for the σ phase alloy 40\% (V) \((\text{Fe}_{2}^{12}\text{V}_{4}^{12}\text{V}_{8}^{14}\text{Fe}_{8}^{14}\text{Fe}_{8}^{14}\text{V}_{8}^{14}\text{Fe}_{8}^{14})\), calculated for \(R_{m}\text{Fe}=2.13, R_{m}\text{V}=1.94\) for variation for \(c/a\) for \(a=\text{const}\) – triangles and for variation for \(a\) for \(c/a=\text{const}\) - circles.
Figure 6. The total energy (Ry / cell) of the Sigma phase of the 40% (V) alloy for various distributions of Fe and V atoms over 5 sublattices as a function of volume, calculated for $R_{mFe}=2.13$, $R_{mV}=1.94$ for variation for “a” for c/a=const. Configuration ($Fe_{2.12}V_{4.15}V_{8.14}Fe_{12}Fe_{14}$) (BC) – rectangles, ($Fe_{2.12}V_{4.15}Fe_{12}V_{8.14}Fe_{14}$) (BD) triangles, ($Fe_{2.12}V_{4.15}Fe_{12}V_{8.14}$) (BE) - rhombuses.

Figure 7. The total energy (Ry / cell) of the Sigma phase of the 40% (V) alloy for various distributions of Fe and V atoms over 5 sublattices as a function of volume, calculated for $R_{mFe}=2.13$, $R_{mV}=1.94$ for variation for “c/a” for a=const. Configuration ($Fe_{2.12}V_{4.15}V_{8.14}Fe_{12}Fe_{14}$) (BC) – rectangles, ($Fe_{2.12}V_{4.15}Fe_{12}V_{8.14}Fe_{14}$) (BD) triangles, ($Fe_{2.12}V_{4.15}Fe_{12}V_{8.14}$) (BE) – rhombuses.
Figure 8. The lattice parameters “a” and “c” as a function of the composition Xv of the sigma phase of the Fe-V.

Figure 9. The mixing energy (Ry/cell) - phase as function of Xv relative to σ - phases of the pure components of the Fe - V system for the ground state.

4. Conclusions
A procedure has been developed for calculating the minimum total energy from two independent parameters of the tetragonal σ -phase lattice. The convergence analysis of the search for the minimum total energy (Ry/cell) of the σ -phase of Fe is carried out. The optimized lattice parameters were
calculated for pure Fe and V. The initial values of the lattice parameters was obtained for $\sigma$–phase of the Fe-V system. Optimized lattice parameters were calculated for Fe$_{0.6}$V$_{0.4}$ and Fe$_{0.4}$V$_{0.6}$ s alloys of the Fe-V system. The first results of quantum-mechanical calculations of the total energy from the sublattices of the $\sigma$–phase as a function of volume are obtained for stable (and metastable) configurations of stoichiometric compositions of Fe$_{0.6}$V$_{0.4}$ and Fe$_{0.4}$V$_{0.6}$

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