DFT modeling of concentration dependences of mixing energy, structural properties and distribution of atomic magnetic moments by Fe-V system sigma-phase lattices for the ground state

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Abstract. The region of existence of the sigma-phase of the Fe-V system was studied. The calculations carried out using the licensed package of quantum mechanical calculations WIEN2k. The dependences of the mixing energy and partial magnetic moments of Fe atoms in alloys of the Fe-V system, located on different sublattices depending on the composition, was obtained.

1. Introduction
The aim of this work is to study the region of existence of the \( \sigma \)-phase of the Fe-V system. The calculations were carried out using a licensed package of quantum mechanical calculations WIEN2k. The authors developed and applied an original algorithm for determining the minimum values of the total energy depending on two external structural variables (parameters of the crystal lattice) [1,2,3]. Previously, the optimized values of the crystal lattice parameters, the formation energies of stoichiometric alloys for the Fe-V system were calculated [2,3,4,5]. The disadvantages of the previously performed calculations were: 1) different values of the initial conditions of calculations (Rm-radii of “cores”, 2) a small value of Kmax - the number of attached plane waves, and 3) non-inclusion of lattice relaxation (i.e., the procedure of minimizing the total energy over internal structural degrees of freedom). In this work, obtained the dependences of the mixing energy and partial magnetic moments of Fe atoms in \( \sigma \)-phase alloys of the Fe-V system for the stoichiometric compositions Fe-33\% V, Fe-40\% V, Fe-53\% V, Fe-60\% V on various sublattices of the \( \sigma \) - phases depending on the composition.

In the present work, we obtained the dependences of the mixing energy and partial magnetic moments of Fe atoms in \( \sigma \) - phase alloys of the Fe-V system for stoichiometric compositions of the corresponding Fe-33 at. \% V, Fe-40 at. \% V, Fe-53 at. \% V, Fe-60 at. \% V located on different sublattices of the \( \sigma \) - phase, depending on the composition.

2. Assessment of lattice parameters \( \sigma \) – phases of pure components
According to [1-3] the initial values of the crystal lattice parameters of metastable \( \sigma \) - phases of pure components a (Fe), c (Fe) and a (V), c (V) were estimated from the approximation of the equality of the occupied volume per atom for both Fe and V in sigma- 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 equal 2.03 a.u. and for cores of V is equal 2.10 a.u. The total energy was minimized according to \([1, 3]\). First, they were minimized by the lattice parameter “a” under the condition \(c = \text{const}\), then by parameter “c” under the condition \(a = \text{const}\). This procedure was repeated until the minimum energy values calculated in different directions were equal (with precision \(δE=10^{-8}\) Ry/cell was chosen as the criterion for the self-consistency). Thus, the optimized values of the lattice parameters (a, c) and total energy were calculated for paramagnetic (PM) V and ferromagnetic (FM) Fe \([6-7]\).

### 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 for pure components and the Vegard rule for the lattice parameters of the \(σ\) – phase depending on the composition \(a(x)\) and \(c(x)\), similar to \([4]\). Thus, the initial (start) values of the lattice parameters were obtained for different stoichiometric compositions of the \(σ\) – phase (among different configurations at fixed composition) in order to find the minimum of total energy for \(σ\) - phase (see Table 2 \(Fe\)-33at.% V, \(Fe\)-40% V, \(Fe\)-53%V, \(Fe\)-60at.% V) in space \(Etot \sim a \sim c\) for stoichiometric chemical compounds of the Fe-V system. The input data on the cores radii \(Rm\) (Fe) and \(Rm\) (V), as well as the exit criteria for \(δE=0.5\) m Ry/Bohr, are presented in Table 1. The energy criterion for end of calculations \(δEtot≈10^{-8}\) Ry/cell is similar to the criterion calculation of the mixing energy equal to \(δEmix=10^{-3}\)Kj/mol, taking into account that

1. \(Emix\) is calculated from three \(Etot\) values (one for compound and two values for pure components)
2. Cell of \(σ\)-phase contains 30 atoms,
3. The conversion factor of energy in units of Ry / atom into units of Kj / mol, of the order of is 1312.75. Thus \(δEmix=3*10^5\) Kj/mol, taking into account that

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En-order the \(σ\)-phase contains 30 atoms,
\]

#### Table 1. Input values of parameters for calculations of alloys with structure \(σ\) – phase

| Configuration | \(Rm(V)\), Bohr | \(Rm(Fe)\), Bohr | \(Kmax\) | \(Force\), mRy/Bohr |
|---------------|----------------|----------------|---------|---------------------|
| \(Fe\)        | --             | 2.03           | 2000    | 0.5                 |
| \(V_{2}\)\(^{12}\)Fe\(^{4}\)V\(^{8}\)\(^{14}\)Fe\(^{8}\)\(^{12}\)Fe\(^{14}\) (AC\(^*\)) | 2.12  | 2.03           | 2000    | 0.5                 |
| \(Fe\(^{2}\)V\(^{4}\)\(^{14}\)Fe\(^{16}\)\(^{10}\)\(^{12}\)V\(^{8}\)\(^{14}\) (BE) | 2.12  | 2.03           | 2000    | 0.5                 |
| \(Fe\(^{2}\)Fe\(^{4}\)V\(^{13}\)Fe\(^{16}\)\(^{12}\)V\(^{8}\)\(^{14}\) (CE) | 2.12  | 2.03           | 2000    | 0.5                 |
| \(V\)         | 2.12           | --             | 2000    | 0.5                 |

*The designation (AC) indicates which sublattices of the sigma phase are filled with vanadium atoms*

Then, the total energy was minimized in the \(E_{tot} \sim a \sim c\) space (the results of calculations on the structural properties of chemical compounds for stable configurations of stoichiometric compositions, see Table 2).

#### Table 2. Equilibrium values of lattice parameters for sigma-phase of the Fe-V system

| Configuration | at.%\(V\) | \(a\), Bohr | \(c\), Bohr | \(c/a\) |
|---------------|-----------|-------------|-------------|--------|
| \(V_{2}\)\(^{12}\)Fe\(^{4}\)V\(^{8}\)\(^{14}\)Fe\(^{8}\)\(^{12}\)Fe\(^{14}\) (AC) | 33        | 16.576999   | 8.6171259  | 0.519824 |
| \(Fe\(^{2}\)V\(^{4}\)\(^{14}\)Fe\(^{16}\)\(^{10}\)\(^{12}\)V\(^{8}\)\(^{14}\) (BE) | 40        | 16.576582   | 8.6967913  | 0.524643 |
| \(Fe\(^{2}\)Fe\(^{4}\)V\(^{13}\)Fe\(^{16}\)\(^{12}\)V\(^{8}\)\(^{14}\) (CE) | 53        | 16.757279   | 8.6412947  | 0.515674 |
| \(V_{2}\)\(^{12}\)Fe\(^{4}\)V\(^{8}\)\(^{14}\)Fe\(^{8}\)\(^{12}\)V\(^{8}\)\(^{14}\) (ACE) | 60        | 16.839668   | 8.7239336  | 0.518059 |
4. Results of calculations of total energies of 4 stoichiometric compositions for σ-phase alloys of the Fe-V system

In this work, in contrast to the works [5], a chemical compound with the structure of sigma-phase composition equal to 53.3 at.% V was added. On the basis of Tables 1 and 2, optimization calculations of the total energy and mixing energy of alloys with the structure of the σ-phase of the Fe-V system were carried out taking into account the relaxation of the crystal lattice. Optimization calculations of the mixing energy of alloys with the structure of the sigma phase of the Fe-V system were obtained from the data in Table 1 and 2 (see Table 4) taking into account the relaxation of the crystal lattice. The distributions of the magnetic moments of atoms components (over the σ-phase sublattices) were calculated for the stoichiometric compositions of the Fe-V system compounds at fixed volume for stable configurations with minimum of values of total energy (see Table 3).

Table 3 Partial magnetic moments at the atoms of crystallographically nonequivalent sublattices, and total magnetic moment of the cell (m_B / cell) for four ordered configurations with Sigma-phase structure in the Fe-V system

| Systems     | mmi1_12(2) | mmi2_15 (4) | mmi3_14(8) | mmi4_12(8) | mmi5_14 (8) | mtot/cell |
|-------------|------------|-------------|------------|------------|------------|-----------|
| Fe-V33AC    | -0.57721   | 1.97848     | -0.5647    | 1.21986    | 2.0135     | 26.63276  |
| Fe-V40BE    | 1.15137    | -0.38392    | 1.8065     | 1.317      | -0.33028   | 21.76472  |
| Fe-V53CE    | -0.14628   | 1.34212     | -0.18417   | 0.2554     | -0.07752   | 4.35572   |
| Fe-V60ACE   | -0.15077   | 1.49114     | -0.23344   | 0.3903     | -0.05274   | 5.71438   |

According to the calculated data presented in Table 3, the dependences of the partial magnetic moment of atoms (m_B / atom) on crystallographically nonequivalent sublattices of the Fe-V-Sigma ordered compounds (Figure 1) and the average magnetic moment atoms (m_B / atom) in stoichiometric compounds with Sigma structures of the Fe-V system were obtained depending on from the composition (Figure 2).

Figure 1. The dependence of the partial magnetic moments atoms (m_B / atom) on crystallographically nonequivalent sublattices of the Fe-V-Sigma ordered compounds of stoichiometric compositions depending on the composition, for the ground state.
The dependence of the total magnetic moment of Fe atoms (m_B / cell) in ordered stoichiometric compound with sigma – phase structure for the Fe-V system for the ground state as function composition.

Table 4 The results of calculations of the stable configuration of the total energy and the mixing energy relative to the sigma phases of pure components with the structure of the sigma phase of the Fe-V system

| Configuration | Energy (Ry/cell) | Energy (Ry/atom) | dE f Ry/atom | dE f Kj/mol |
|---------------|-----------------|-----------------|--------------|-------------|
| Sigma-Fe      | -76368.03381    | -2545.601127    | 0.00         | 0           |
| V_2^{12}Fe_4^{14}V_8^{14}Fe_8^{12}Fe_8^{14} | -69898.82406 | -2329.960802 | -0.01267757 | -16.642 |
| Fe_2^{12}V_4^{14}Fe_8^{14}Fe_8^{12}V_8^{14} | -68604.87784 | -2286.831066 | -0.01354173 | -17.777 |
| Fe_2^{12}Fe_4^{14}V_8^{14}Fe_8^{12}V_8^{14} | -66017.10304 | -2200.570101 | -0.013778231 | -18.087 |
| V_2^{12}Fe_4^{14}V_8^{14}Fe_8^{12}V_8^{14} | -64723.15815 | -2157.438605 | -0.012882919 | -16.912 |
| Sigma-V       | -56959.26357    | -1898.642119    | 0.00         | 0           |

According to the results of table. 4, the dependence of the mixing energy of the σ phase on the composition of Xv relative to the σ phases of the pure components of the Fe - V system for the ground state (Figure 3) was obtained.

The obtained results of calculations of the total energies for the sigma - phase were tested on calculating the differences in structural energies between the bcc and sigma - phases of pure components and compared with the results obtained in [6]. For vanadium, according to our calculations, E_{tot}(bcc-V) - E_{tot}(sigma –V) = - 3.68 Kj / mol, in comparison -4.9 Kj / mol [6]; for Fe E_{tot}(FMbcc-Fe) - E_{tot}(FMsigma –Fe) = -8.43 Kj / mol, in comparison with -17.6 Kj / mol. [6]. The obtained difference in the results for Fe is possibly due to the fact that our calculations were performed (in order to reduce the calculation time) at K = 2000, while in [6] the calculations were performed at K = 5000.
5. Conclusion

In this work, the dependence of the mixing energy of the $\sigma$ phase on the composition of Xv relative to the $\sigma$ phases of the pure components of the Fe - V system for the ground state was calculated and the selection of structural properties for stable configurations of the $\sigma$ phase. The distributions of the magnetic moments of Fe atoms (over the $\sigma$ -phase sublattices) for stoichiometric compositions of compounds of the Fe-V system depending on the volume for the same initial simulation conditions for the compositions and considering the lattice relaxation for the-phase of alloys in stable configurations were calculated.

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