Application of super cells for quantum-mechanical calculations of the mixing enthalpy of the BCC-phase of the Fe-V system for the basic state

A L Udovsky and M V Kupavtsev
Baikov Institute of Metallurgy and Material Sciences, Moscow, Russian Federation
E-mail: audovskiy@imet.ac.ru, mikhail_77@mail.ru

Abstract. In this work, the super-cells were used for quantum mechanical calculations of the mixing enthalpy of the BCC phase of the Fe-V system for the ground state. The values of total energy were calculated using 16-th and 54-atomic super-cells for both clean components and alloys. The mixing enthalpy (ΔH) for the BCC phase was calculated on four 16- and 54-atomic super-cells in the vicinity of pure components, on the basis of which the dependence of the concentration ΔH for BCC alloys in the ferromagnetic state of the Fe-V system of the ground state was built.

1. Introduction
In order to test the results of quantum mechanical calculations (QMC) of the enthalpy of formation (ΔH) of a chemical compound with a sigma-phase structure in the Fe-V system [1-3] and to assess its chemical stability relative to the bcc phases of both pure components and relative to BCC solutions in this system, taking into account the change in temperature starting from the ground state, it becomes necessary to calculate ΔH BCC - solutions depending on the composition.

Taking into account that experimental studies for bcc solutions are usually carried out in the region of relatively high temperatures in order to achieve bringing the alloys to an equilibrium state in reasonable times comparable to the time of experiments when the alloys are in a paramagnetic state. Whereas QMC ΔH are carried out for the ground state, when alloys based on BCC –Fe are in the ferromagnetic (FM) state. QMC ΔH is calculated for the ground state when alloys based on bcc –Fe are in the ferromagnetic (FM) state. Mössbauer spectroscopy shows that bcc alloys of both Fe- (Cr, V) systems based on Fe have a short-range order [4], the value of which, depending on the composition, changes its sign. Taking into account the significant size factor \( \varepsilon_V = \frac{V_{OL(V)} - V_{OL(Fe)}}{V_{OL(Fe)}} = 1.22 \), it is problematic to use the coherent potential method (CPA) to calculate ΔH of the BCC of a disordered solution of the Fe-V system. It is more correct to take into account the relaxation of the crystal lattice using the QMC method. Since there are static displacements of Fe and V atoms relative to the sites of an ideal crystal lattice, due to the presence of the size factor, and different values of the elastic moduli \( B(V) = 156.2 \text{ GPa} \) and \( B(Fe) = 167 \text{ GPa} \) = 0.938 [5], the application of the variation method clusters [6-7] for a disordered BCC Fe\(_{1-x}\)V\(_x\) solution is incorrect. The lengths of the “edges” of the clusters will have different lengths (different lengths of the edges of the cluster will lead it to an irregular shape, for example, deviate from the regular shape of the tetrahedra), depending on the composition and temperature.
Since the clusters will take an irregular shape, taking into account that the “average” or effective modulus of elasticity of the solution depends on the alloy composition, therefore, the shape and size of the clusters will also depend on the composition, leading to the nonequivalence of such “non-rigid” clusters for different compositions.

2. Calculation method
In order to take into account the change in the total energy depending on the composition in this work, in accordance with the method proposed in [8], we used supercells containing a different number of BCC lattices. We used 16 and 54 atomic cells, each of which contained for one impurity atom, while the rest contained matrix atoms, which is equivalent to the alloy compositions 6.25, 1.85, as well as 93.75 and 98.15 at. %. In this work, QMC was performed using the WIEN2k licensed software package for the FM state. For QMC, we used:

1) the maffin-tin radii Rmt (Fe) = 2.03 and Rmt (V) = 2.12;
2) the accuracy for self-consistent energy calculations was $\Delta E_{\text{tot}} = 10^{-7-8}$ Ry / cell , Rkmax = 8;
3) the number of plane waves $k = 2000$;
4) the relaxation of the lattice in terms of forces was also taken into account with an accuracy of $\Delta F = 0.5$ mRy / bohr (see Table 1).

Table 1. Input values of the calculation parameters for 16 and 54 atomic supercells of alloys containing one atom of impurity with the structure of the BCC phase.

| Cell | Rm , Bohr | Kmax | Force, mRy/Bohr | n, cell |
|------|-----------|------|----------------|--------|
| Fe   | 2.03      |      | 0.5            | 16     |
| Fe   | 2.03      |      | 0.5            | 54     |
| V    | 2.12      |      | 0.5            | 16     |
| V    | 2.12      |      | 0.5            | 54     |

3. Calculation results
In accordance with the developed methodology [1-3], the initial values of the crystal lattice parameters of stable BCC - phases of pure components a (Fe) and a (V) for a standard bcc cell were obtained. As the initial values of the lattice parameters for supercells V16 and V54 (Fe16 and Fe54), we took the doubled and triple lattice parameters calculated previously for the corresponding BCC lattice. Starting from the initial values of the lattice parameters by minimizing the total energy, the volume-optimized lattice parameters and total energies of 16 and 54 atomic super-cells of pure components with the structure of the BCC phase of the Fe-V system were calculated, see Table 2.

The total energy was minimized according to [1, 3] along the “a” of the supercell. This procedure was repeated until the minimum energy values coincided, until the criterion for exiting the cycle in terms of energy, equal to to $\Delta E = 10^{-8}$ Ry / cell, was fulfilled. Thus, the optimized values of the lattice parameters (a) and the minimum values of the total energies were calculated for both the paramagnetic (PM) BCC phase V and the ferromagnetic BCC Fe phase (see Table 2).

Table 2. Consistency of the results of calculations of the lattice parameters and total energies of 16 and 54 atomic supercells of pure components with the structure of the bcc phase of the Fe-V.

| Cell | a, Cell (bohr) | V, Cell (bohr3) | Etot, Ry/cell | Etot Ry/atom |
|------|----------------|-----------------|---------------|-------------|
| V16  | 11.3311033     | 1454.84455      | -30378.318075 | -1898.6448797 |
| V54  | 16.9874698     | 4902.14436      | -102526.82315 | -1898.644873 |
| Fe16 | 10.6779146     | 1217.47299      | -40729.721542 | -2545.6075964 |
| Fe54 | 16.0182137     | 4110.00400      | -137462.80991 | -2545.6075909 |
Table 2 shows the consistency of the obtained energy calculation results for 16 and 54 atomic supercells for both pure components:

\[
\frac{E_{\text{tot}}(54-FM-Fe)}{54} - \frac{E_{\text{tot}}(16-FM-Fe)}{16} = -0.0000055 \quad \frac{\text{Ry}}{\text{atom}} = -7.22 \quad \frac{\text{J}}{\text{mol}}
\]

\[
\frac{E_{\text{tot}}(54-V)}{54} - \frac{E_{\text{tot}}(16-V)}{16} = 0.0000067 \quad \frac{\text{Ry}}{\text{atom}} = 8.8 \quad \frac{\text{J}}{\text{mol}}
\]

To calculate the total energy, depending on the composition, in this work we used supercells with alloy compositions equal to 6.25, 1.85 at. % both in the vicinity of the 1st and 2nd components. The results of the calculations are presented in Table 3 for both the lattice parameters of the alloys (Figure 1) as well as the minimum values of the total energy for supercells, Table 3 and Figure 2.

**Table 3.** The values of the total energies of stable (equilibrium) configurations of the BCC phase of the Fe-V system for the ground state.

| Configuration | Energy (Ry/cell) | Energy (Ry/atom) | a (cell), bohr | V (cell)bohr³ |
|---------------|-----------------|-----------------|---------------|--------------|
| Fe15-1V       | -40082.80989    | -2505.17562     | 10.74745      | 1241.41499   |
| Fe53-1V       | -136815.89945   | -2533.62777     | 16.081067     | 4158.57537   |
| V15-1Fe       | -31025.352043   | -1 939.0845     | 11.228283     | 1415.598192  |
| V53-1Fe       | -103173.91290   | -1910.62802     | 16.965629     | 4883.26083   |

**Figure 1.** Results of optimization of the lattice parameters of the BCC phase, calculated by minimizing the total energy over the volume for supercells containing 16 and 54 atoms, both for pure components and for alloys containing one impurity atom in each of the supercells, the Fe - V system.
The results of quantum mechanical calculations of the total energy and mixing energy for the BCC phase (relative to the energies of the BCC phases of pure components) of Fe-V system alloys for the ground state were obtained using, for example, the relation (1)

$$\Delta E_{mix}^{bcc}(x_i) = \frac{E^{bcc}(Fe_{16}V_{16})}{16} - \left\{ \left(1 - \frac{1}{16}\right) \cdot E^{bcc}(Fe_{16}) + \frac{1}{16} \cdot E^{bcc}(V_{16}) \right\}$$

and are presented in comparison with the results of experiments [9] for alloys in the paramagnetic state in Figure 2. In (1) at $x_i = 1 = x_V = 0.0625$; similar ratios were used for compositions $x_V \approx 0.0185; 0.09325; 0.98148$. The details of processing the calculated data described in detail in [8].

Figure 2. Results of quantum-mechanical calculations of the enthalpy of mixing ($\Delta H$) for ferromagnetic bcc phases of alloys of the Fe-V system for the ground state in comparison with experimental data for alloys in the paramagnetic state at 1623K [9] and the results of calculations performed in [10].

Figures 2 and 3 show qualitative agreement of the dependence $H(x)$ of the QMC results of this work with the experimental data [9], although the calculations were performed for FM alloys for the ground state, while the experimental data [9] were obtained for paramagnetic alloys at 1623K. Comparison of the QMC results of this work with the calculated data [10] carried out within the exact EMTO method for ferromagnetic alloys for compositions at $x(V) = 0.2$ and 0.8 approximately equal to $\Delta H = -3$ and -5 KJ/mol, respectively, which is also shown in Figure 2 and Figure 3.
Figure 3. Construction of the interpolation concentration dependence of the enthalpy of mixing for bcc solutions of the Fe-V system for the ground state and comparison with the experimental data obtained at 1623 K in [9].

Acknowledgments
The research was financially supported the financial support of the RFBR Fund in the framework of a scientific project № 19-03-00530

References
[1] Kupavtsev M V and Udovsky A L 2019 Ninth International Scientific Conference “Chemical Thermodynamics and Kinetics ” Collection of scientific papers pp 335–6
[2] Kupavtsev M V and Udovsky A L 2020 J. Phys.: Conf. Series 1431 012056
[3] Udovsky A L and Kupavtsev M V 2020 J. Phys.: Conf. Ser. 1658 012067
[4] Grafutin V I et all 2017 J. Min. Metall Sect. B-Metall 53 (3) B 399–405
[5] Chen Q and Sundman B 2001 Acta mater 49 947–61
[6] Kikuchi R 1951 Phys. Rev. 81 998
[7] Kikuchi R 1998 J. Phase Equilibria 19 412
[8] Udovsky A L 2021 Analytical-interpolation method for describing the concentration dependence of the enthalpy of mixing of the BCC phase using quantum-mechanical calculations of supercells in Fe -(Cr, V, Mo) systems 2021 Eleventh International Scientific Conference “Chemical Thermodynamics and Kinetics” Collection of scientific papers
[9] Spencer P J and Putland F H 1973 Iron. Steels. Inst. 211 293–97
[10] Kissavos A E, Simak S I, Abrikosov I A, Olsson P and Vitos L 2006 Comp. Mater. Sci. 35 1–5