Quantum-mechanical calculations of mixing enthalpy of the bcc phase of the Fe-Mo system for the ground state

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Abstract. The structural energies, formation enthalpies and bulk elastic moduli of bcc iron and molybdenum in the Fe–Mo system, are calculated for further use in the calculations of the bcc / bcc + Fe₂Mo Laves phase boundary at low (room) temperatures.

1. Introduction
Molybdenum alloying is often used to harden ferritic steels. However, the stability region of bcc solutions enriched by the Fe atoms is limited by the presence of the C14 type Fe₂Mo Laves (λ-) phase in the Fe–Mo system. So, for developments of ferritic steels in particular, it is necessary to know the binary or ternary phase diagrams (for example, Fe-Cr-Mo). But, in order to calculate the α/α + λ boundary of the Fe-Mo system, see figure 1, one need to know the thermodynamic properties of bcc and Fe₂Mo phases.

Figure 1. The experimental phase diagram of the Fe-Mo system.
Therefore, for calculations between the bcc phase and Laves phase the Gibbs energy as a function of concentration and temperature for bcc phase as well as the Gibbs energy of Fe₂Mo phase as a temperature dependence are needed to be known. An experimentally obtaining of thermodynamic properties as a function of concentration and temperature for these phases is accompanied by big difficulties as a follow of both the short concentration range of bcc phase (see figure 1) and that in the 300-1000K temperature interval diffusion processes are very slow, and almost impossible to reach an equilibrium state.

For solutions of these problems around the room temperature different approaches were used in the last ten years. It’s a phenomenological method in which an extrapolation of experimental high temperature data is used, as well as applying of physic-empirical models and ab-initio approach in the vicinity of the ground state. And a complex utilizing quantum- mechanical calculations together with the CALPHAD method by fixing to experimental data of phase equilibria for calculation of unknown model parameters. But, the using the procedure of fixing to experimental high temperature data of phase boundaries as it is in the CALPHAD method [1] can lead to significant errors due to the low accuracy of these experimental data. In particular, when extrapolating experimental high-temperature data to the range of relatively low temperatures of 300–600 K, in which both ferritic and austenitic steel grades are used. In this regard, it is of considerable interest, both from a methodological point of view and in practical applications, to use quantum mechanical calculations not only to simulate the presence and stability of the Fe₂Mo intermetallic compound, but also to calculate the enthalpy of mixing of the bcc phase depending on the composition, primarily for ground state (at T = 0 K).

2. Calculation methodology

It should be noted that taking into account the presence of a large size linear factor \( \varepsilon_{\text{lin}} = (a_{\text{Mo}} - a_{\text{Fe}})/a_{\text{Fe}} = (3.147-2.8665)/2.8665 = 0.098 \), that equals to almost 32% of relative differences of atom volumes, it is very problematic to use the coherent potential method for a bcc disordered solution of the Fe-Mo system. While the more practical approach is the taking into account the relaxation of crystal lattice in the frame of a use of quantum mechanics calculations. Due to the existence of different values of the static displacements of iron and molybdenum atoms relative to the sites of the ideal crystal lattice caused by the presence of:
1) big size factor;
2) different masses of atoms, differing from each other by about 2 times, and also;
3) different values of bulk modulus \( B(\text{Mo})/B(\text{Fe})=265\text{GPa}/167\text{GPa}=1.59 \) [2],
therefore, it seems unreasonable to use the cluster variation method [3-4] for disordered the bcc Fe\(_{1-x}\)Mo\(_x\) solution.

Due to the fact that the lengths of the “edges” of the clusters will have different lengths (different lengths of the edges of the cluster will lead to an irregular shape, for example, deviate from the correct shape of the tetrahedral), and the lengths of the edges of the clusters will vary depending on the composition. Therefore, the clusters will take an irregular shape, taking into account that the “average” or effective modulus of elasticity of the solution also varies depending on the composition of the alloy. Therefore, the shape and size of the clusters will also depend on the composition, leading to the non-equivalence of such “no rigid” clusters for different compositions.

Changes of the total energy due to the composition change, in this work, were modelled by the use of super cells containing a different numbers of atoms: 16-, 54- and 128- atoms in a super cell. Each of these contained the one alloying atom, that reflected the composition of 6.25, 1.85 and 0.78 at. %. The quantum mechanical calculations were carried out by the WIEN2k package.

The total energies of bcc Fe and Mo phases were calculated under the following conditions: the muffin-tin radius \( R_{\text{mt}} \) were set as \( R_{\text{mt}}(\text{Fe}) = 2.05 \) and \( R_{\text{mt}}(\text{Mo}) = 2.15 \), \( R_{\text{max}} = 8 \), and the irreducible Brillouin zone was modelled by the 12x12x12 and 10x10x10 k-point mesh.

The calculated total energies of ferromagnetic bcc Fe and paramagnetic bcc Mo as functions of volume are shown in figure 2.
Figure 2. The total energies of ferromagnetic bcc Fe (left) and paramagnetic bcc Mo (right) as a function of volume. The calculations were conducted with 12x12x12 k-point mesh.

By using the optimization procedure with applying the Murnaghan’s equation of state (EOS) the equilibrium lattice parameters $a = 2.8307 \, \text{Å}$ for Fe and $a = 3.1608 \, \text{Å}$ for Mo were obtained, which deviate from the experimental values by 1.2 and 0.4% respectively. The values of calculated bulk modulus were 199 GPa for Fe and 261 GPa for Mo that deviate from experimental values ($B(\text{Fe}) = 166.7 \, \text{GPa} \, [2]$ and $B(\text{Mo}) = 265 \, \text{GPa} \, [2]$) by 19% and 7% respectively. These data together with the other calculated physical characteristic (lattice parameter, bulk modulus ($B$), the first derivative of $B$ by pressure ($BP$)) for different super cells are listed in Table 1.

Table 1. Comparison of the calculated ground state physical properties for the ferromagnetic bcc Fe and paramagnetic bcc Mo with experimental data obtained for 2 atoms cell and 16 and 54 atoms super-cells.

| Element | Property | 2 atoms cell | 16 atoms cell | 54 atoms cell |
|---------|----------|--------------|---------------|--------------|
| **Fe: a_calc, Å** | | | | |
| | 2.8307 | 2.82985$^a$ | 2.8292$^b$ |
| | 2.82965$^b$ | | |
| **a_exper. Å** | 2.8665 | | | |
| **B(Vo), GPa** | 199.02 | 197.818$^a$ | 199.5339$^b$ |
| | | | |
| **B_exper, GPa** | 166.7$^5$ | | | |
| **dB/dP** | 6.048 | 6.0254$^a$ | 6.2693$^b$ |
| | | | |
| **E(Vo), Ry/atom** | -2545.607474 | -2545.419944$^a$ | -2545.6074698$^b$ |
| | | | |
| **Mo: a_calc, Å** | 3.1608 | 6.32072opt$\rightarrow$3.16035$^a$ | 3.1604$^b$ |
| | 3.147 | 6.3217opt$\rightarrow$3.16085$^b$ | |
| **a_exper. Å** | 3.147 | 3.1603$^a$ | |
| **B(Vo), GPa** | 260.6 | 260.1589$^a$ | 261.089$^b$ |
| | | | |
| **B_exper, GPa** | 265$^5$ | | | |
| **dB/dP** | 3.8852 | 4.26298$^a$ | 4.2323$^b$ |
| | | | |
| **E(Vo), Ry/atom** | -8099.176711 | -129586.830731 Ry/cell$^b$ | -129586.830651 Ry/cell$^a$ | -437355.552884 Ry/cell$^b$ | -8099.176905 Ry/atom$^b$ |
| | | $\Rightarrow$-8099.17692 Ry/atom$^a$ | $\Rightarrow$-8099.176916 Ry/atom$^a$ | |

$^a$ The calculations were conducted with 10x10x10 k-point mesh
b) The calculations were conducted with 12x12x12 k-point mesh.

Figure 3. The total energies of ferromagnetic bcc Fe$_{53}$Mo$_{47}$ super cell (left) and paramagnetic bcc Mo$_{53}$Fe$_{47}$ super cell (right) as a function of volume. The calculations were conducted with 12x12x12 k-point mesh.

In order to convolution of the calculated data for various compositions of super-cells containing 16, 54, and 128 sites, respectively, and in each such site one atom was putted, the following formal description of the mixing enthalpy was applied, which remains invariant with respect to the transition from system A–B to system B–A

\[
\Delta H(x_1, x_2) = x_1 x_2 \{ x_1 A_1 + x_2 B_1 + x_1 x_2 (x_1 A_2 + x_2 B_2 + \ldots) \} 
\]

(1)

This ratio was used in the work [5], by the first author of this article, as the basis of arguments for the subsequent orthogonalization procedure for the displaced Yacobi polynomials to describe the concentration dependences of various properties of alloys of binary closed systems in order to create databases. In (1) $A_1$, $B_1$, $A_2$, $B_2$ are constants which needed to be calculated; $x_1$ and $x_2$ are concentrations of the first and the second component respectively.

For the closed system

\[
x_1 + x_2 = 1
\]

(2)

Choosing the concentration of the 2-component as an independent variable and restricting ourselves only to linear terms in curly brackets and omitting the lower indices, we obtain

\[
\Delta H(x_1, x_2) = (1 - x) x \{ (1 - x) A + x B \}
\]

(3)

By taken the first derivative in composition of relation (3)

\[
\frac{\partial \Delta H(x_1, x_2)}{\partial x} = (1 - 4x + 3x^2)A + x(2 - 3x)B
\]

(4)

taking the limits in the neighborhood of pure components, that is, when $x \rightarrow 0, x \rightarrow 1$.

One could obtain

\[
\text{Lim } \{ \frac{\partial \Delta H(x)}{\partial x} \}_{x=0} = A; \quad \text{Lim } \{ \frac{\partial \Delta H(x)}{\partial x} \}_{x=1} = -B
\]

(5)

From the obtained relation (5), it follows that the initial slopes of the mixing enthalpy in the vicinity of pure components allow one to determine the concentration dependence in the entire concentration range of alloy compositions – equation (3). It is such a procedure that allows the use of quantum-
mechanical calculations of changes in the enthalpy of mixing for super-cells in the vicinity of compositions near pure components, bcc Fe and Mo in this case. Having obtained these limiting values for the concentration slopes of the mixing enthalpy in the 1st approximation, we can then use the second approximation to use the more complex concentration dependence of the mixing enthalpy depending on the composition by “stitching” these concentration slopes of the mixing enthalpy, and to calculate the values of all parameters by the least squares method and more the complicated concentration dependence of enthalpy of mixing.

3. Calculated results

According to the previous section, in order to use the calculation results for the closed system of Fe-Mo and plot the results depending on the composition in one general graph, it should be taken into account that they should be given per mole atoms or dividing by the number of atoms in one mole, equal to the Avogadro number, i.e. they must be presented per atom. Therefore, all physical calculated properties for these different super-cells are given per atom.

![Figure 4](image_url)

**Figure 4.** The calculated mixing enthalpy values for the phases of different super-cells Fe$_{127}$Mo$_1$, Fe$_{53}$Mo$_1$, Fe$_{15}$Mo$_1$ and Fe$_{1}$Mo$_{53}$, Fe$_{1}$Mo$_{15}$ for the ground state (left figure) and a fragment for super-cells Fe$_{127}$Mo$_1$, Fe$_{53}$Mo$_1$, Fe$_{15}$Mo$_1$ for iron-rich alloys (right figure).

Similarly, all physical calculated properties for different super-cells are given per atom for pure components in table 1, as well as the calculated values of mixing enthalpies for different super-cells containing one impurity atom for bcc alloys of the Fe-Mo system on figure 3.

By interpolating the obtained values of the formation enthalpies calculated for super-cells using the more complete formula (1) under the condition $A_2 = B_2$. As a result, we obtain the interpolation dependence presented in figure 5 (left fragment) taking into account the trend line. Using the coefficients for the trend curve, as a result, we can construct the concentration dependence of the mixing enthalpy for disordered bcc solutions of the Fe-Mo system for the ground state (figure 5 - the right fragment). The calculated results of the mixing enthalpy and its parameters for the bcc Fe-Mo alloys at the ground state are shown in figures 4 and 5.
Figure 5. Calculated parameters of mixing enthalpy for bcc Fe-Mo alloys (in the left) and the mixing enthalpy of bcc dH(x) for the Fe-Mo system at the ground state, at T=0K, (in the right).

4. Conclusion
An analytical – interpolation method is proposed using quantum mechanical calculations of the total energy for a series of super-cells, containing one impurity atom in the matrix, in order to construct the concentration dependence of the enthalpy of mixing for the ground state. This method was applied to calculate the enthalpy of mixing depending on the composition for the bcc phase of the Fe-Mo system.

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