The comparison of different approaches to the modeling of the structural properties \( \sigma \)-phase of Fe-Cr system

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Abstract: The three- sub-lattice model (3SLM) for description of atom’s distribution of two components with different coordination numbers (12, 14 and 15), into \( \sigma \)-phase structure depended on composition and temperature is depicted in this paper. Energetic parameters of 3SLM were calculated by fitting procedure fixed to results obtained by ab-initio calculations conducted for paramagnetic states of differently ordered complexes stayed at the sigma-phase’s crystal structure for Fe-Cr system at 0 K. Respective algorithm and computer program have allowed to calculate an atom distribution of components upon the sub-lattices of \( \sigma \)-phase at 300 – 1100 K. The temperature dependences of filling atoms on the model three sub-lattices for alloys compositions 40, 50 and 60 at. % Fe was calculated. There is satisfactory agreement between calculated results and the experimental data obtained by neutron and structural research methods. The equilibrium between BCC solutions and \( \sigma \)-phase of Fe-Cr system was calculated. The satisfactory consent of results of calculation with experimental data for education temperature \( \sigma \)-phases from BCC–solution and some divergences with experiments is received at 800 K.

1. Introduction
The crystal lattice of sigma-phase contains 5 sub-lattice in which are placed 30 atoms possessing various coordination of the next neighbors (12, 14 and 15). The last ten years of the sigma-phase became object of modeling of numerous quantum and mechanical calculations [1-6] which are applied to calculations of energies of communication and a mixture enthalpy at 0K for the ordered complexes. The analysis of results of numerous calculations on modeling of structural, magnetic and thermodynamic properties of alloys with structure of sigma-phase showed that there are more many not solved problems. In particular, yet it was not possible to carry out calculations of total energies of communication, equilibrium parameters of a lattice, the volume module of elasticity, the partial magnetic moments of atoms sigma-phase taking into account equilibrium static mixtures of atoms from different sub-lattice from sigma-phase. Especially there is open a question of establishment of influence of static mixtures on magnetic properties of the atoms located in five sublattice of sigma-phase, and the average magnetic moment depending on structure.

2. The model formulation for \( \sigma \)-phase
In this work, in order to describe the atom component distributions depending on alloy composition and temperature into the sigma-phase structure the real structure of sigma phase have been modeled by
3 sub-lattices structure. This simplification is caused by to provide possibility of the decision of system of the equations state, received as a result of minimization of a functional of free energy of mixture on internal (configuration) degrees of freedom. According to 3SLM the real structure of \( \sigma \)-phase \( \text{A}_2\text{B}_4\text{C}_8\text{D}_8\text{E}_8\text{F}_8 \) (including 5 sub-lattices) was replaced by 3 sub-lattices. All of the model’s sub-lattices are being filled by atoms of two components with coordination numbers (12, 14 and 15).

\[
a^{(12)} = a^{(A)} + a^{(D)} = 10 \\
a^{(14)} = a^{(C)} + a^{(E)} = 16 \\
a^{(15)} = a^{(B)} = 4.
\]

The Gibbs free energy of mixing of \( \sigma \)-phase of alloys with regard to \( \sigma \)-phases of both components according to 3SLM is equal

\[
\Delta G^\sigma (x, T) = \gamma_{12} \cdot \gamma_{15} \cdot \delta E_{12}^{12} + \gamma_{12} \cdot \gamma_{14} \cdot \delta E_{14}^{14} + \gamma_{12} \cdot \gamma_{15} \cdot \delta E_{12}^{15} + \gamma_{14} \cdot \gamma_{15} \cdot \delta E_{14}^{12} + \gamma_{14} \cdot \gamma_{15} \cdot \delta E_{14}^{14} + \gamma_{14} \cdot \gamma_{15} \cdot \delta E_{14}^{15} + \gamma_{15} \cdot \gamma_{15} \cdot \delta E_{15}^{12} + \gamma_{15} \cdot \gamma_{15} \cdot \delta E_{15}^{14} + \gamma_{15} \cdot \gamma_{15} \cdot \delta E_{15}^{15} + \gamma_{12} \cdot \gamma_{15} \cdot \ln(\gamma_{15}^2) + \gamma_{14} \cdot \gamma_{15} \cdot \ln(\gamma_{15}^2) + \gamma_{15} \cdot \gamma_{15} \cdot \ln(\gamma_{15}^2) \right] \\
R \cdot T \left[ a^{12} \left( \gamma_{12} - \ln(\gamma_{12}^2) \right) + a^{14} \left( \gamma_{14} - \ln(\gamma_{14}^2) \right) + a^{15} \left( \gamma_{15} - \ln(\gamma_{15}^2) \right) \right],
\]

\[
\Delta G^\sigma (x, T) = \gamma_{12} \cdot \gamma_{15} \cdot \delta E_{12}^{12} + \gamma_{12} \cdot \gamma_{14} \cdot \delta E_{14}^{14} + \gamma_{12} \cdot \gamma_{15} \cdot \delta E_{12}^{15} + \gamma_{14} \cdot \gamma_{15} \cdot \delta E_{14}^{12} + \gamma_{14} \cdot \gamma_{15} \cdot \delta E_{14}^{14} + \gamma_{14} \cdot \gamma_{15} \cdot \delta E_{14}^{15} + \gamma_{15} \cdot \gamma_{15} \cdot \delta E_{15}^{12} + \gamma_{15} \cdot \gamma_{15} \cdot \delta E_{15}^{14} + \gamma_{15} \cdot \gamma_{15} \cdot \delta E_{15}^{15} + \gamma_{12} \cdot \gamma_{15} \cdot \ln(\gamma_{15}^2) + \gamma_{14} \cdot \gamma_{15} \cdot \ln(\gamma_{15}^2) + \gamma_{15} \cdot \gamma_{15} \cdot \ln(\gamma_{15}^2) \right] \\
R \cdot T \left[ a^{12} \left( \gamma_{12} - \ln(\gamma_{12}^2) \right) + a^{14} \left( \gamma_{14} - \ln(\gamma_{14}^2) \right) + a^{15} \left( \gamma_{15} - \ln(\gamma_{15}^2) \right) \right],
\]

\[
3. The method of calculations
\]

According to the equation (1) functional of Helmholtz energy of mixture of sigma-phase the equation depends on external arguments (concentration of one of components and temperature) and from internal parameters (\( \gamma_{12}, \gamma_{15} \)) – configuration degrees of freedom.

The system of the equations of state was received by a way of minimization of a functional of free energy of Helmholtz (1) (an alloy depending on structure, temperature and two independent internal parameters (\( \gamma_{12}, \gamma_{15} \)) - the part of filling of atoms two sorts of components for three sub-lattices of inter-metallic compound) on independent internal degrees of freedom at the fixed values of temperature and alloy structure. Equilibrium values of internal parameters of model (at constant values of structure of an alloy and temperatures) are as the decision of system of equations of state (2a) at observance of conditions of local stability an inequality (2b).

\[
\begin{align*}
\frac{d^2\Delta G^\sigma (x,T)}{dy_{12}^{12}} & = 0 \\
\frac{d^2\Delta G^\sigma (x,T)}{dy_{15}^{15}} & = 0 \\
\det \begin{vmatrix} \frac{d^2\Delta G^\sigma (x,T)}{dy_{12}^{12}dy_{12}^{12}} & \frac{d^2\Delta G^\sigma (x,T)}{dy_{12}^{12}dy_{15}^{15}} \\ \frac{d^2\Delta G^\sigma (x,T)}{dy_{15}^{15}dy_{15}^{15}} & \frac{d^2\Delta G^\sigma (x,T)}{dy_{15}^{15}dy_{15}^{15}} \end{vmatrix} & > 0.
\end{align*}
\]

Using the set equation of material balance transition to oblique-angled system of coordinates (\( \gamma_{12}, \gamma_{15} \)) was carried out at the fixed value of composition of an alloy, then carrying out transition since the beginning to Cartesian, and then to polar system of coordinates with a pole choice in a point (\( \gamma_{12}^2 = 0, \gamma_{15}^2 = 0 \)).
It allowed to present, first, system of the equations of state (2a) in orthogonal system of coordinates, and, secondly, to carry out matrix diagonalization (2b). Transition to polar system of coordinates at the fixed structure and temperature allowed to parametrize of system (2b) and to carry out dividing of roots of system (2a). Execution performance (2b) allowed finding areas of local stability in space of internal parameters of model. For system (2a) at each fixed value of composition (x) one of components and temperatures (T) received the decision of system of the equations (2a) which allowed describing concentration dependences of distribution of atoms of components on modeling sub-lattice of sigma-phase. Authors was developed original algorithm and the program for the numerical decision of system of the equations of state (2a).

4. The calculation of energetic parameters of model
A set of equations described the Gibbs free energies of $\sigma$-phase (in relation to meta-stable $\sigma$-phases of pure components) for compositions of $\sigma$-phase being a base solution which equal to compositions of ordered complexes of $A_{12}B_{14}C_{18}^{15}D_{8}^{12}E_{8}^{14}$ – type for $\sigma$-phase [7] for which in turn quantum-mechanical calculations of formation energies [1, 4] were carried out, was constituted in order to calculate the 3SLM energetic parameters. The linear system of the equations of relationships [7] between the 3SLM energetic parameters and results of quantum-mechanical calculations of formation energy of the ordered complexes of type $A_{12}B_{14}C_{18}^{15}D_{8}^{12}E_{8}^{14}$ was obtained as a result. Thus the restrictions were lifted as the inherent quantum mechanical calculations (calculations energies of formation of complexes completely ordered only when 0K) and phenomenological models (a large number of energy parameters, the inability to describe the distribution of the component atoms over the sub-lattices $\sigma$-phase) thermodynamic properties of alloys with $\sigma$-phase structure.

The solution of linear system concerning the 3SLM energetic parameters allowed receiving the following values of energetic parameters of model presented in table 1.

| $\Delta E_{12}^{12}$ | $\Delta E_{12}^{14}$ | $\Delta E_{12}^{15}$ |
|----------------------|----------------------|----------------------|
| $-6500 \ (J/mol.)$  | $520 \ (J/mol.)$     | $-7020 \ (J/mol.)$  |

| $\Delta E_{14}^{12}$ | $\Delta E_{14}^{14}$ | $\Delta E_{14}^{15}$ |
|----------------------|----------------------|----------------------|
| $-1500 \ (J/mol.)$  | $-13520 \ (J/mol.)$ | $7540 \ (J/mol.)$   |

| $\Delta E_{15}^{12}$ | $\Delta E_{15}^{14}$ | $\Delta E_{15}^{15}$ |
|----------------------|----------------------|----------------------|
| $5460 \ (J/mol.)$   | $-10660 \ (J/mol.)$ | $-26000 \ (J/mol.)$ |

5. The calculation results
The solution of system of the state equations allows to describe structural (distributions of atoms of components on three model sub-lattices) and thermodynamic properties of sigma-phase depending on alloy composition and temperature. Developed 3SLM algorithm and the computer program were applied to modeling of distribution of Fe and Cr atoms on model sub-lattices of sigma-phase depending on composition and temperature.

Figures 1-2 shows a comparison of the calculated distribution of the atoms over the sub-lattices depending on the composition obtained in this work, both with Joubert data [6] on, so their comparison with the experimental data at $T = 500$ and 1000 K. We also calculated the temperature dependence of filling atoms on the model three sub-lattices of $\sigma$-phase for alloy compositions 40, 50 and 60 at. % Cr (figures 3-5).
Figure 1. Comparison of the distribution of Fe atoms over the sub-lattices obtained in this study with data Joubert [6] and their collation with experimental data at 1000 K [9-11].

Figure 2. Comparison of the distribution of atoms over the sub-lattices obtained in this study with data Joubert [6] at 500 K.
Figure 3. Temperature dependence of filling atoms on the three sub-lattices model for the alloy composition 40 at. % Fe.

Figure 4. Temperature dependence of filling atoms on the three sub-lattices model for the alloy composition of 50 at.% Fe, the experiment at 1000 K [9-11].

Figure 5. Temperature dependence of filling atoms on the three sub-lattices model for the alloy composition 60 at. % Fe.
The results obtained allowed to calculate the equilibrium between the bcc - and $\sigma$- phases (figure 6).

![Figure 6. The fragment of BCC-Sigma equilibrium of Fe-Cr system.](image)

6. Conclusion
For 3SLM were calculated concentration and temperature dependences of the structural (filling model sub-lattice atoms of components) and thermodynamic properties of the sigma phase and evaluated equilibria between the sigma - and bcc - phases in the system Fe-Cr.

Acknowledgments
The research was supported by grants for RFBR projects 09-03-00983-a, 13-03-00482-a and by Chemistry and Materials Science Branch of the Presidium of Russian Academy of Sciences, project OKhNM-02.

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