

Letter to Editor

## **MODELING OF STRUCTURAL AND THERMODYNAMICS PROPERTIES OF SIGMA-PHASE FOR THE 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. There is satisfactory agreement between calculated results and the experimental data obtained by neutron and structural research methods. Obtained results demonstrate satisfactory agreement between calculated and experimental data of BCC solutions and sigma – phase of the Fe-Cr system stayed at an equilibrium state.*

**Keywords:** structural properties; thermodynamics; phase diagram; modeling; sigma-phase; Fe-Cr alloys

### **1. Introduction**

The problem of computational materials design is interdisciplinary. It includes well-known experimental data description and prediction of unknown thermodynamic and physical properties as well stable as meta-stable phases of n-component systems. Now there are three problems which don't allow developing an effective method of forecasting of various properties of stable and meta-stable phases in multi-component systems. The first problem is that energetic and physical properties of meta-stable phases can be obtained only by ab-initio calculations limited by now in obtaining of equilibrium properties only at 0K [1-5]. It should be noted that experimental values of parameters for a tetragonal lattice of sigma – phases were used in papers on ab-initio calculations of energy properties of sigma – phases for the Cr-Fe system over the time of 10-15 years [1-2, 4-5, 7-10]. One exception is a paper [11] in which sigma – phase calculations of pure iron and pure chrome were carried out and calculations for the ordered complexes of the Fe-Cr system were carried out too but with the help of a total energy minimized as well on lattice parameters of a tetragonal phase  $a$  and  $c/a$  (without use of experimental values of lattice parameters of sigma – phase) and minimized as on the magnetic moments of Fe and Cr atoms located in different sub-

lattices of sigma-phase of those the ordered complexes. However, in paper [11] on account of considerable expenses of compute time only three ordered complexes with structure of sigma-phases were calculated.

The second problem follows from below. The Gibbs potential temperature dependences of stable and meta-stable phases (i.e. stability parameters) as a first approximation equated in differences of enthalpies and entropies between BCC- and sigma – phases of pure components, are considered to be used in calculation of entropy differences of pure components as adjusted parameters and were used for phase diagram calculations of the Fe-Cr [1, 2], Cr-Co [4], Ni-V [6], Re-W [9] systems containing the sigma– phase. But, the entropy terms of Gibbs energy differences between elements stayed at BCC- and sigma – phase structures, obtained in papers [1-2, 4], by the way, have still to be adjusted to the experimental phase equilibrium data. Nevertheless, as follow from a theorem about invariance of the system of the phase equilibrium equations with regard to an algebraic adding of those equations to the Gibbs's energies of considered phases introduced as linear functions depended on composition and on arbitrarily temperature depended coefficients [12-13]. That the adjustment procedure of unknown temperature terms to temperature dependences of differences of Gibbs's

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energies between various phases of pure components is not an equivocal procedure at the solution of an inverse problem (calculation of thermodynamically equilibrium properties of alloys from experimental data). Thus, procedure of the adjustment can result in erroneous values for differences of entropies between different phases of pure components as is shown in [2, 4] and as an outcome can result in erroneous values of excess thermodynamic properties of alloys in various phases.

The third essential point of used approaches do appear from generalized calculations (broadly using in the last 25-30 years in the world literature) of thermodynamic properties of phases and phase equilibrium of n-component systems are based mainly on a joint processing of experimental data of two groups: on thermodynamic properties of phases and on phase equilibria (points or tie-lines) of phase diagram (so-called CALPHAD - a method of research of phase equilibrium). Regarding structural properties, first of all - experimental data of atom distributions of components between sub-lattices of phases with complicated crystal structure, there are only isolated instances of their account in the general scheme of CALPHAD method [3-6, 9].

This complex approach developed by authors is briefly described in this work applicable to the Fe-Cr system which contains, according to experimental data, the following phases: sigma - a phase, BCC - solutions as in ferromagnetic, including a short range order and in paramagnetic conditions, and FCC - solutions. The purpose of the present article is attempt to model a generalization structural and thermodynamic of sigma - phases depended on structure of alloys and on temperature, and an assessment of their coupled influence on phase equilibrium of solutions on the basis of sigma - phase with BCC - solutions without taking into account a short range order, at least.

## 2. The model formulation for $\sigma$ - phase

The crystal lattice of sigma-phase contains 5 sub-lattices in which 30 atoms possessing of different coordination numbers of the nearest neighbors (12, 14 and 15) are placed. The last of ten years the sigma-phase became an object of numerous quantum-mechanical modeling [1-2, 4] which are applied to calculations as well of cohesive energy of pure components in BCC- and in sigma-phases and as a mixture enthalpy at 0K for the ordered complexes. The analysis of results of numerous model calculations of structural, magnetic and thermodynamic properties of alloys with structure of sigma-phase have showed that there are many not solved problems. In particular, it is not possible yet to carry out calculations of total energies, equilibrium

parameters of a lattice, the bulk module of elasticity, the partial magnetic moments of atoms of sigma-phase taking into account equilibrium static displacements of atoms settled in different sub-lattices of sigma-phase. Especially there is an open question of establishment of influence of static mixtures on magnetic properties of the atoms located in five sub-lattices of sigma -phase, and on the average magnetic moment depending on structure. Though the first steps in this direction was make and partially theoretically solution were obtained in paper [14] for ferromagnetic BCC - phases as well of pure iron as of the Fe-Cr alloys.

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 allows obtaining the solution of system of state equations by a minimization of a mixture free energy functional on internal (configuration) degrees of freedom. Since the obtained system of state equations consists of transcendental equations there are not, generally speaking, any analytical methods to find the solution.

According to 3SLM the real structure of s-phase  $A_2^{12}B_4^{15}C_8^{14}D_8^{12}E_8^{14}$  (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). Thereby, we have relationships between number atoms in model and real sub -lattices for sigma- phase in the manner of the following equations:

$$\begin{aligned} a^{(12)} &= a^{(A)} + a^{(D)} = 10 & \alpha^{(12)} &= a^{(12)} / (a^{(12)} + a^{(14)} + a^{(15)}) \\ a^{(14)} &= a^{(C)} + a^{(E)} = 16 & \alpha^{(14)} &= a^{(14)} / (a^{(12)} + a^{(14)} + a^{(15)}) \\ a^{(15)} &= a^{(B)} = 4 & \alpha^{(15)} &= a^{(15)} / (a^{(12)} + a^{(14)} + a^{(15)}) \end{aligned} \quad (1)$$

The Gibbs free energy of mixing of s- phase of alloys with regard to s- phases of both components according to 3SLM is equal (the details of the mathematical calculations possible to see in paper [14]):

$$\begin{aligned} \Delta^{\sigma} G^{\sigma}(x, y_2^{12}, y_2^{15}, T) &= y_1^{12} \cdot y_2^{12} \cdot \delta E_{12}^{12} + y_1^{12} \cdot y_2^{14} \cdot \delta E_{12}^{14} + y_1^{12} \cdot y_2^{15} \cdot \delta E_{12}^{15} \\ &+ y_1^{14} \cdot y_2^{12} \cdot \delta E_{14}^{12} + y_1^{14} \cdot y_2^{14} \cdot \delta E_{14}^{14} + y_1^{14} \cdot y_2^{15} \cdot \delta E_{14}^{15} + \\ &y_1^{15} \cdot y_2^{12} \cdot \delta E_{15}^{12} + y_1^{15} \cdot y_2^{14} \cdot \delta E_{15}^{14} + y_1^{15} \cdot y_2^{15} \cdot \delta E_{15}^{15} + \\ &R \cdot T \cdot \left[ \alpha^{12} (y_1^{12} \cdot \ln(y_1^{12}) + y_2^{12} \cdot \ln(y_2^{12})) + \right. \\ &\left. \alpha^{14} (y_1^{14} \cdot \ln(y_1^{14}) + y_2^{14} \cdot \ln(y_2^{14})) + \right. \\ &\left. \alpha^{15} (y_1^{15} \cdot \ln(y_1^{15}) + y_2^{15} \cdot \ln(y_2^{15})) \right] \end{aligned} \quad (2)$$

where energetic parameters of the model (f.e.  $\delta E_{12}^{14}$ ) are linear combinations of pair inter-atomic energies changed between atoms settled in any of the three sub-lattices (it's noted by superscript, f. e.  $y_1^{12}$ ) and atoms settled in around of any of three sub-lattices

(it's noted by subscript, f.e.  $y_2^{14}$ ) under replacement of matrix atoms by alloying atoms.

$$\begin{aligned} \delta E_{12}^{12} &= 6 \cdot (a^{12})^2 [\delta E_1^{12,12} + \delta E_2^{12,12}], \delta E_{12}^{14} = 12 \cdot (a^{12})^2 \delta E_1^{12,14} + 9 \cdot (a^{14})^2 \delta E_2^{14,12}, \delta E_{12}^{15} = 6 \cdot (a^{12})^2 \delta E_1^{12,15} + 6 \cdot (a^{15})^2 \delta E_2^{15,12}, \\ \delta E_{14}^{12} &= 9 \cdot (a^{14})^2 \delta E_1^{14,12} + 12 \cdot (a^{12})^2 \delta E_2^{12,14}, \delta E_{14}^{14} = 15 \cdot (a^{14})^2 [\delta E_1^{14,14} + \delta E_2^{14,14}], \delta E_{14}^{15} = 4 \cdot (a^{14})^2 \delta E_1^{14,15} + 8 \cdot (a^{15})^2 \delta E_2^{15,14}, \\ \delta E_{15}^{12} &= 6 \cdot (a^{15})^2 \delta E_1^{15,12} + 6 \cdot (a^{12})^2 \delta E_2^{12,15}, \delta E_{15}^{14} = 8 \cdot (a^{15})^2 \delta E_1^{15,14} + 4 \cdot (a^{14})^2 \delta E_2^{14,15}, \delta E_{15}^{15} = (a^{15})^2 [\delta E_1^{15,15} + \delta E_2^{15,15}]. \end{aligned}$$

Entropy of mixing in the equation (2) is written down in Gorsky – Bragg – Williams approximation.

The condition of material balance is (3)

$$a^{12} y_2^{12} + a^{14} y_2^{14} + a^{15} y_2^{15} = 30 \cdot x, \tag{3}$$

where  $x$  – composition of the second component in the Cr-Fe system,  $y_i^{j,k}$  – ( $i=12, 14, 15$ ) mole fractions of the first and second component in sub-lattice model of the  $s$ - phase.

### 3. Calculation method

According to the equation of material balance (3) the functional of free energy of mixing of sigma-phase (2) depends on external arguments (one of component concentration for a closed system and temperature) and on internal parameters () – named as configuration degrees of freedom.

The system of the state equations was obtained by minimization of the functional of free energy of mixing (2) (which depends on alloy composition, crystal structure, temperature and two independent internal parameters ( $y_2^{12}, y_2^{15}$ ) – the mole fractions of two sorts of atoms which fill three sub-lattices of inter-metallic compound) on independent internal degrees of freedom at the fixed temperature and alloy structure.

Equilibrium conditions of internal parameters of the model (under condition of permanency of alloy composition and temperature) is calculated by the solutions of the system of state equations (4a) under observance of local stability conditions (4b).

$$\begin{cases} \frac{d^\sigma \Delta^\sigma G^\sigma(x,T)}{dy_2^{12}} = 0 \\ \frac{d^\sigma \Delta^\sigma G^\sigma(x,T)}{dy_2^{15}} = 0 \end{cases} \tag{4a} \quad \det \begin{vmatrix} \frac{d^2 \Delta^\sigma G^\sigma(x,T)}{dy_2^{(12)2}} & \frac{d^2 \Delta^\sigma G^\sigma(x,T)}{dy_2^{(15)2}} \\ \frac{d^2 \Delta^\sigma G^\sigma(x,T)}{dy_2^{(12)2}} & \frac{d^2 \Delta^\sigma G^\sigma(x,T)}{dy_2^{(15)2}} \end{vmatrix} > 0 \tag{4b}$$

By using the equation of material balance (3) a transition to oblique-angled coordinate system  $y_1^{12}, y_2^{15}$

was carried out under the fixed value of alloy composition, then a next transition was carried out at first to Cartesian and then to polar coordinate system with a pole selected in the point ( $y_2^{12} = 0, y_2^{15} = 0$ ).

It allows as well presenting the system of the state equations (4a) in orthogonal coordinate and as carrying out a diagonalization of matrix (4b). A transition to the polar coordinate system under the fixed alloy composition and temperature permits to parameterize the system (4b) and to carry out a root separation of the system (4a). The inequality (4b) allows finding local stability areas in a space of internal parameters of the model. Under every fixed temperature and composition of one of component the resulting solution of the system of the state equations (4a) allows describing the atom concentration dependences distributed on the model sub-lattices of sigma-phase.

Authors have developed an original algorithm and a computational program for obtaining a numerical solution of the system of the state equations (4a).

### 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  $A_2^{12}B_4^{15}C_8^{14}D_8^{12}E_8^{14}$  – type for  $s$ - phase (see table 1) for which in turn quantum-

mechanical calculations of formation energies [2,4] were carried out, was constituted in order to calculate the 3SLM energetic parameters.

The linear system of the equations of relationships

**Table 1.** The input data of quantum-mechanical calculations of energetic parameters (mRy/atom) the Cr-Fe system for ordered complexes with the model Sigma - phase structure at 0K

Model of complexes	Filling options of sub-lattices in the ordered complexes for model sigma-phase.	x(Fe)	$\sigma \Delta^\sigma E^\sigma$
Cr12Fe14Cr15	$y_1^{12} = 1, y_2^{12} = 0, y_1^{15} = 0, y_2^{15} = 1, y_1^{14} = 1, y_2^{14} = 0$	0.133	0.8
Fe12Cr14Cr15	$y_1^{12} = 0, y_2^{12} = 1, y_1^{15} = 1, y_2^{15} = 0, y_1^{14} = 1, y_2^{14} = 0$	0.333	-10.8
Fe12Cr14Fe15	$y_1^{12} = 0, y_2^{12} = 1, y_1^{15} = 0, y_2^{15} = 1, y_1^{14} = 1, y_2^{14} = 0$	0.467	-9.2
Cr12Fe14Cr15	$y_1^{12} = 1, y_2^{12} = 0, y_1^{15} = 1, y_2^{15} = 0, y_1^{14} = 0, y_2^{14} = 1$	0.533	-7.8
Cr12Fe14Fe15	$y_1^{12} = 1, y_2^{12} = 0, y_1^{15} = 0, y_2^{15} = 1, y_1^{14} = 0, y_2^{14} = 1$	0.667	-5
Fe12Cr14Fe15	$y_1^{12} = 0, y_2^{12} = 1, y_1^{15} = 1, y_2^{15} = 0, y_1^{14} = 0, y_2^{14} = 1$	0.867	-4
(CrFe)12Fe14Fe15	$y_1^{12} = 1/5, y_2^{12} = 4/5, y_1^{15} = 0, y_2^{15} = 1, y_1^{14} = 1/2, y_2^{14} = 1/2$	0.933	-1.8
Fe12Cr14(FeCr)15	$y_1^{12} = 0, y_2^{12} = 1, y_1^{15} = 1, y_2^{15} = 0, y_1^{14} = 1/2, y_2^{14} = 1/2$	0.6	-10

(5) between the 3SLM energetic parameters and results of quantum-mechanical calculations of formation energy of the ordered complexes of type  $A_2^{12}B_4^{15}C_8^{14}D_8^{12}E_8^{14}$  was obtained as a result. On base of this ground the system of the equations was obtained for a search of initial parameters of model at 0K.

$$\left\{ \begin{array}{l} \sigma \Delta^\sigma E^\sigma (x = 0.133) = \delta E_{12}^{14} + \delta E_{12}^{15} + \delta E_{14}^{15} = 0.8 \\ \sigma \Delta^\sigma E^\sigma (x = 0.333) = \delta E_{14}^{12} + \delta E_{15}^{12} = -10.8 \\ \sigma \Delta^\sigma E^\sigma (x = 0.467) = \delta E_{14}^{12} + \delta E_{14}^{15} = -9.2 \\ \sigma \Delta^\sigma E^\sigma (x = 0.533) = \delta E_{12}^{14} + \delta E_{15}^{14} = -7.8 \\ \sigma \Delta^\sigma E^\sigma (x = 0.667) = \delta E_{12}^{14} + \delta E_{12}^{15} = -5.0 \\ \sigma \Delta^\sigma E^\sigma (x = 0.867) = \delta E_{15}^{12} + \delta E_{15}^{14} = -4.0 \\ \sigma \Delta^\sigma E^\sigma (x =) = \frac{4}{25} \cdot \delta E_{12}^{12} + \frac{1}{5} \cdot \delta E_{12}^{14} + \frac{1}{5} \cdot \delta E_{12}^{15} = -1.8 \\ \sigma \Delta^\sigma E^\sigma (x =) = \frac{1}{2} \cdot \delta E_{14}^{12} + \frac{1}{4} \cdot \delta E_{14}^{14} + \delta E_{15}^{12} + \frac{1}{2} \cdot \delta E_{15}^{14} = -10.0 \end{array} \right. \quad (5)$$

The solution of linear system (5) concerning the 3SLM energetic parameters allowed to receive the following values of energetic parameters of model presented in table 2.

**Table 2.** The data of energetic parameters of 3SLM model for alloys with the s-phase structure (Joule/mole)

$\Delta E_{12}^{12} = -6500$	$\Delta E_{12}^{14} = 520$	$\Delta E_{12}^{15} = -7020$
$\Delta E_{14}^{12} = -19500$	$\Delta E_{14}^{14} = -13520$	$\Delta E_{14}^{15} = 7540$
$\Delta E_{15}^{12} = 5460$	$\Delta E_{15}^{14} = -10660$	$\Delta E_{15}^{15} = -26000$

### 5. The calculation of stability parameters of model

Differences of structural total energies between BCC-and sigma-phases for iron and Chromium at 0K were calculated with application of quantum-mechanical methods in different papers [1, 2, 15] – see table 3. However, the system of the state equations

**Table 3.** Values of differences energies between sigma – and BCC – phases and bulk elasticity modules of Sigma – and of BCC- phases of the pure components calculated in different papers.

Fe		Cr		References
E <sup>Sigma</sup> - E <sup>BCC</sup> , kJ/mol				
40,5		20,2		[1] FLAPW, GGA
43,2		30,3		[2]
17,6		13,2		[15]
B <sup>BCC</sup>	B <sup>Sigma</sup>	B <sup>BCC</sup>	B <sup>Sigma</sup>	
209,6 GPa	330,6 GPa	205 GPa	253,8 GPa	[17]

weren't given in these works. Only in one work [17] the system of the state equations and, therefore, bulk elasticity modules were calculated at 0K both for BCC - phases, and for sigma-phases for iron and chrome which are also brought in table 3.

Being limited for simplification by only oscillatory contribution to differences entropies between BCC-and sigma-phases in Debye model approach it is received for Fe:

$$S_{Fe}^{BCC} - S_{Fe}^{\sigma} \approx 3R \ln \frac{\theta_{D,Fe}^{\sigma}}{\theta_{D,Fe}^{BCC}} = (3R/2) \ln \frac{B_{Fe}^{\sigma}}{B_{Fe}^{BCC}} = 5,683 \text{ J/mol.K} \quad (6)$$

and for Cr:

$$S_{Cr}^{BCC} - S_{Cr}^{\sigma} = 2,624 \text{ j/mol} \cdot K \quad (7)$$

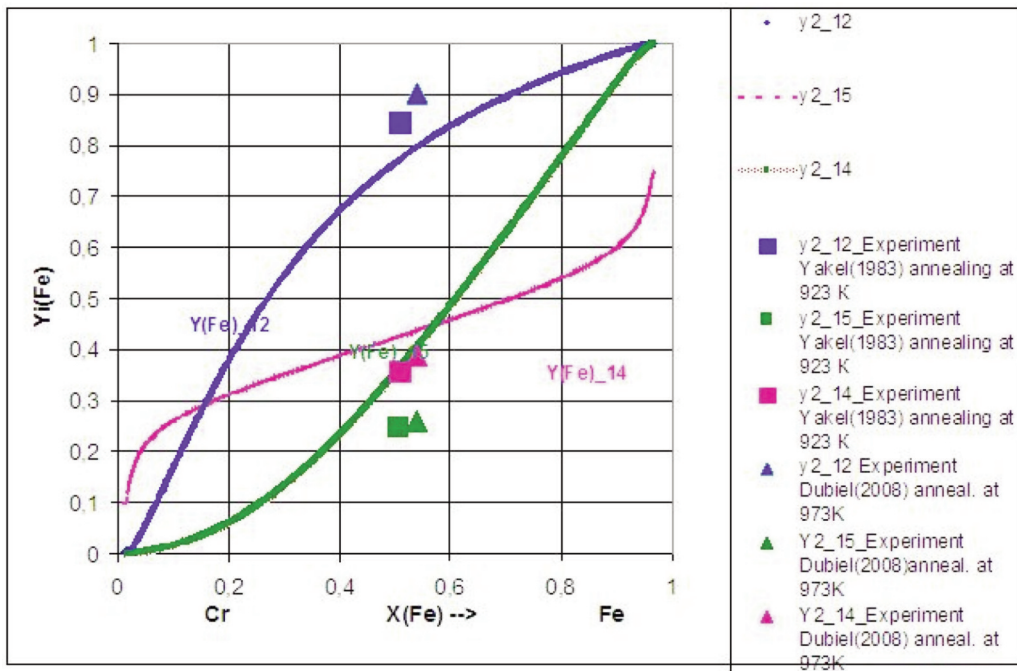
### 6. The calculation results

The obtained values of energetic parameters of model allow passing to the solution of system of the state equations (4a). It is obvious that the solution of system of the state equations (3a) depend as well on alloy composition and temperature as on parameters. Therefore 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. The test of the model depicted on fig. 1 shows the comparison at 900K between the calculated concentration dependences of Fe atoms filling all of three- model sub-lattices of sigma- phase and experimental data obtained on alloys with the compositions of 50,8 at. %Fe annealed at 923K [16] and of 53,8 at. %Fe annealed at 973K [3], in terms of considered model and according to ratios (1).

From fig. 1 follow that there is the satisfactory agreement between calculated and experimental data obtained by different authors [3,16]. In the range of stable alloys of sigma-phase the sub-lattices with coordination of the atoms equal to 12 is mainly filled by Fe -atoms, and Cr- atoms filling the sub-lattices with coordination of atoms equal to 14 and particular, at alloy composition equal to 50 at. % Fe the sub-lattice with coordination of the atoms equal to 12 is filled by Fe atoms at two times more than the sub-lattice with coordination of the atoms equal to 14 and 15.

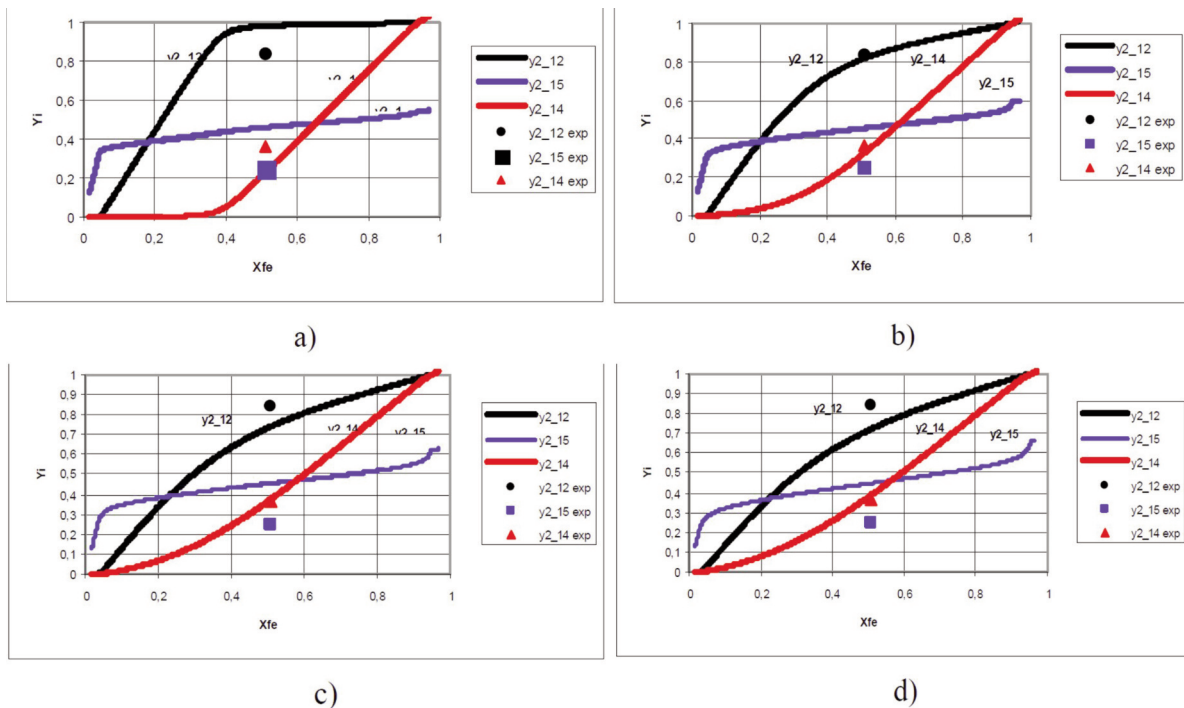
Calculated results of distribution of Fe- atoms in the Cr-Fe system on model sub-lattices of sigma-phase at T=300,1100 K are shown on fig. 2. The comparison





**Figure 1.** The comparison of concentration calculations of Fe atom distributed on three- sublattice of the sigma-phase model at 900K with experimental data (by taking into account the binding equations (1) for an alloy of composition equal to 50,8 at. %Fe annealed at 923K according to paper [16] are marked by rectangles and an alloy composition equal to 53,8 at. %Fe annealed at 973K according to paper [3] are marked by triangles).

between calculated results and experiment data has shown a good agreement.



**Figure 2.** The Fe atom sub-lattice distribution of  $\sigma$ -phase of the Cr-Fe system at  $T=300$  K (a),  $700$  K (b),  $1000$  K (c),  $1100$  K (d).

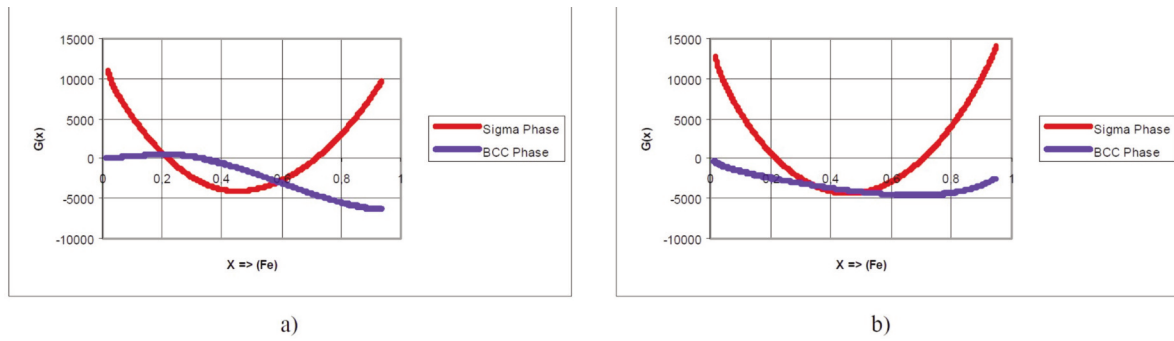


Figure 3. Concentration dependences of the Gibbs free energy of mixing for BCC (blue curve) and Sigma (red curve) phases of the Cr-Fe system at  $T=300$  K (left) and  $1000$  K (right).

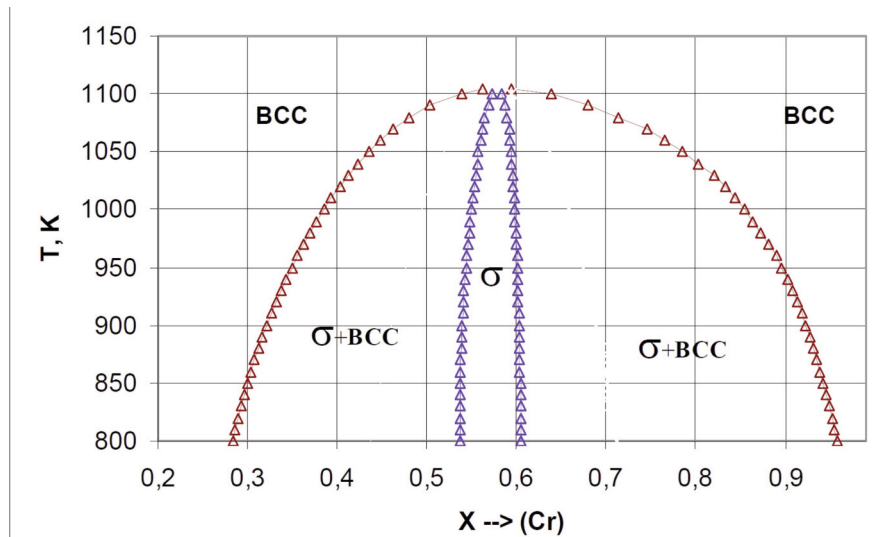


Figure 4. The fragment of BCC-Sigma equilibrium of Fe-Cr system

Calculations of phase equilibrium between BCC - and sigma- phases of alloys of the Fe-Cr system which are presented on fig. 4 have been carried out by using as well stability parameters for the entropy differences between BCC- and sigma-phases of pure iron and chrome that have been reported in [15] and by as values of the entropy differences calculated by formulas (6) and (7) and by as dependences of mixture energies of BCC- solutions and sigma - phase for alloys (see Fig. 3) too.

The homogeneity area of a sigma- phase of alloys of Fe-Cr system at 950K located in the middle between 923K and 973K temperatures at which the studied alloys are annealed according [15,3] and the width of the area is equal about to 5 atom's percent that correlated with experimental data, see fig. 4.

However, the calculation results show that location of the phase border limiting the homogeneity area of a sigma- phase by shifting the two-phase (bcc-rich Cr + sigma-phase) field to the Cr side of the diagram comparatively of 50 % atomic composition.

It is possible to believe that it is caused by essentially big relation of the calculated bulk modules of elasticity for Fe  $B_{Fe}/B_{Fe}^{BCC} = 1,57$  in comparison with relation of the calculated bulk modules of elasticity for Cr  $B_{Cr}/B_{Cr}^{BCC} = 1,238$  that leads to a bigger difference of entropies between BCC-and sigma- phases for Fe.

## 7. Conclusion

In the presented work the statistics-thermodynamic of third- sublattice model was developed for the description of distribution of atoms of components in sigma- phase of binary system. The algorithm of calculation and the computer program for the solution of system of the state equations depending on composition of alloys and temperature was developed. The energetic parameters of model were calculated by using results of quantum-mechanical calculations of formation energy of the ordered complexes with crystal structure of the sigma

- phase.

Thus, restrictions inherent as well to quantum-mechanical calculations (calculations of formation energies of ordered complexes at 0 K), and as to phenomenological models (a large number of energetic parameters, impossibility of the description of distributions of atoms of components on sub-lattices of sigma- phase) on modeling of thermodynamic properties of alloys with structure of sigma- phase where removed.

The complex approach developed by authors allows to eliminate, first, the restrictions of application of quantum-mechanical calculations to thermodynamics and to phase diagram of n-component systems due to application of statistics-thermodynamic model and by using the physics-empirical models allowed to link the harmonious properties obtained by quantum-mechanical calculations at 0K. Secondly, it allows to expand CALPHAD method applications. Namely, the generalized and coordinated description of a number of physical, in particular, structural (distribution of atoms of components on sub-lattices of chemical compounds with a difficult crystal structure) and thermodynamic properties and of phase equilibrium of alloys of two - and three-component systems including computer calculations for a prediction of thermodynamic and physical properties, and also of phase equilibriums of n-component systems, is emerged.

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### References

- [1] J. Havrankova, J. Vrest'al, L.G. Wang, M. Sob, Phys. Rev. B 63 (2001) 174104 p. 2001
- [2] J.Houserova, M. Friak, M. Sob, J. Vrestal, Comp. Mater. Science. 25 (2002) 562 and J. Houserova, J. Vrestal, M. Friak, M. Sob. CALPHAD 22 (2002) 513.
- [3] J. Cieslak, M. Reissner, W. Steiner, S.M. Dubiel. Phys. Stat. Sol. (a) 205 (2008) 1794.
- [4] J. Vrestal, A. Kroupa, M. Sob. Comp. Mater. Sci. 38 (2006) 298.
- [5] A.E. Kissavos, S.I. Simak, P. Olsson, L. Vitos, I.A. Abrikosov. Comp. Mater. Sci. 35 (2006) 1.
- [6] A. Watson, F.H. Hayes. J. Alloys and Comp. 320 (2001) 199.
- [7] M. Sluiter, K. Esfarjani, Y. Kawazoe. Phys. Rev. Lett. 75 (1995) 3142.
- [8] C.Berne, M. Sluiter, Y. Kawazoe, T. Hansen, A. Pasturel. Phys. Rev. B 64 (2001) 144103.
- [9] S.G. Fries, B. Sundman. Phys. Rev. B 66 (2002) 012203.
- [10] J. Cieslak, J. Tobola, S.M. Dubiel, and W. Sikora. arXiv 1010.3856.v.1 [cond-mat.mtrl-sci. 19 Oct. (2010) 1-10.
- [11] E.A. Kabliman, A.A. Mirzoev, A.L. Udovskii. The Phys. of Metals and Metallography, 108 (2009) 435. Original Russian Text E.A. Kabliman, A.A. Mirzoev, A.L. Udovskii., published in Fizika Metallov i Metallovedenie, 108 (2009) 461.
- [12] A.L. Udovsky. Solid State Phenomena 138 (2008) 241.online at <http://www.scientific.net>© (2008) Trans Tech Publications, Switzerland Online available since 2008/Mar/07
- [13] A.L. Udovsky. Proc. of Joint European Thermodynamics Conf. IX. Saint-Etienne. June 12-15, 2007. Ecole Nationale Supérieure des Mines. Eds. B.Guy and D.Tondier. (2007) p.189-193.
- [14] A.L. Udovskii. ISSN 0036 0295, Russian Metallurgy (Metally), (2011), 889-909. © Pleiades Publishing, Ltd., 2011. Original Russian Text © A.L. Udovskii. 2011, published in Metally, (2011) 5, p. 121-143.
- [15] M.H.F. Sluiter. CALPHAD, 30 (2006) 357. (PAW=projected augmented wave – method, VASP-package, GGA, 2 optimization procedure, the first on volume, later on all crystallographic degrees of freedom: as {a, a/c}, for as displacements of atoms for s- phase ).
- [16] H.L. Yakel. Acta Crystallography. B 39 (1983) 20.
- [17] E.A. Kabliman (calculation by using program WIEN2k) in.: A.L. Udovsky. Scientific report on RFBR- project 06-03-00352\_a (2008).