

## **ENERGETICS AND PHASE DIAGRAMS OF Fe-Cr AND Co-Cr SYSTEMS FROM FIRST PRINCIPLES**

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### **Abstract**

*The first principles computations of the total energies of complex phases have been addressed recently. The structural energy differences, calculated by FLAPW (Full potential augmented plane wave) method, enable us to utilize a more complete physical information about total energy of intermetallic phases and to propose a new model for their thermodynamic description.*

*Our approach is based on the two-sublattice model, similarly as for solid solution phases, but the structural energy differences for end-members in the metastable or unstable structures are obtained by means of first-principles electronic structure calculations.*

*Phase diagrams of Fe-Cr and Co-Cr systems containing the intermetallic sigma-phase (5 inequivalent lattice sites, 30 atoms in repeat cell) are described here as an example of application of our new model.*

**Keywords:** first principles calculations, lattice stabilities, complex structures, phase diagrams

## 1. Introduction

Improvement of traditional materials and development of new ones could be hardly possible without coupling thermochemistry and phase diagram calculation as it is done in the CALPHAD (CALculation of PHase Diagram) technique. The most important goal of this approach is to characterize all of the possible phases in the system, stable, metastable and unstable ones, by their Gibbs energy values over the widest possible range of temperature, pressure and composition. The thermochemical basis of the CALPHAD method then relies explicitly on the notion that the equilibrium phase composition arises as the result of minimisation of Gibbs energy in closed system at constant external conditions [1].

Thermodynamic modelling (parametrization) of solution phases is one of the most important steps of the CALPHAD method [2]. Most of the models used to describe this are incorporated in the Compound Energy Formalism (CEF). In CEF the Gibbs energy for a phase  $G^f$  is given by the general formula:

$$G^f = \sum_i y_i^o G_i^f + \Delta G^{id} + \Delta G^E + \Delta G^{mag} \quad (1)$$

where the first term in Eq.(1) gives the contribution of the Gibbs energy of formation of the considered phase from the standard reference state of the pure constituents (so called lattice stability difference), the second term corresponds to ideal mixing of components in the phase, the third part is called excess Gibbs energy and the remaining term includes a contribution of some special physical properties (e.g. magnetic transformation).

The total Gibbs energy of the system is then given by:

$$G^f = \sum_i w^f G^f \quad (2)$$

where  $w^f$  represents the weight fraction of the phase in the system.

## 2. Experimental evaluation of lattice stability

Gibbs energies of formation of simple phases (bcc, fcc, hcp...) were subject of concerted effort of Scientific Group of ThermoData Europe (SGTE) in the eighties and they were published in 1991 by A.T. Dinsdale [3].

More complicated situation concerns the complex intermetallic structures. For

modelling of intermetallic phases in ternary and more component systems, it is often necessary to know the lattice stability difference between the standard Gibbs energy of that phase (which is usually hypothetical for pure constituents) and Gibbs energy of its standard element reference state (SER) when the phase could be treated as solution phase (slow change of mixing Gibbs energy with composition). This task can be solved experimentally for the metastable or unstable structures by extrapolation of experimental values of thermodynamic properties of phases from the real solution region to the pure constituents (end-members). This procedure was demonstrated for the sigma phase (tetragonal lattice with 30 atoms in repeat cell in 5 inequivalent positions) in the papers of Hayes and Kubitz [4,5]. From the analysis of assessed enthalpy and entropy data for bcc Fe-Cr phase as well as of phase boundaries for (sigma+bcc) Fe-Cr, those authors found the following limits of values of  $\Delta H^{\text{sigma} \rightarrow \text{bcc}}$  characterizing the lattice stability of sigma-phase: for pure Cr from +1825 to -2052 J.mol<sup>-1</sup>, and for pure Fe from -84 to -4670 J.mol<sup>-1</sup>. Analogously, in Co-Cr the limits of  $\Delta H^{\text{sigma} \rightarrow \text{bcc}}$  for pure Cr were from +3052 to -2354 J.mol<sup>-1</sup>, and for pure Co from +47610 to +51800 J.mol<sup>-1</sup> (with Co bcc as standard state). All values were gained using an estimate of entropy change  $\Delta S_{\text{sigma} \rightarrow \text{bcc}}$  for pure constituents equal to -2.0 J.K<sup>-1</sup>.mol<sup>-1</sup> (the first value) and to -6.0 J.K<sup>-1</sup>.mol<sup>-1</sup> (the second value).

It is apparent that a range of “acceptable” equilibrium diagrams could be reproduced using variety of lattice stability equations. The reason why it is possible to use a range of lattice stability plus Gibbs energy coefficients for sigma phase is basically a consequence of the form of phase boundaries together with the shape of the Gibbs energy in the sigma phase field. “Lattice stabilities” can be changed at will provided appropriate compensation is made to the coefficients in equations for  $\Delta H$  and  $\Delta S$ . Changing these coefficients might alter the overall shape of Gibbs energy in sigma phase field considerably but these changes in regions where sigma phase is metastable are of no significance in reproducing the binary equilibrium diagram.

Hayes and Kubitz have extended their calculations in [5]. Using the Fe-Cr and Co-Cr data [6-11], they arrived to the following results for  $\Delta H^{\text{sigma} \rightarrow \text{bcc}}$  in pure constituents (Co fcc as standard state):

- a) equating integral Gibbs energies of mixing of bcc phase and sigma phase at mid-point of (sigma+bcc) phase field, the values of  $\Delta H^{\text{sigma} \rightarrow \text{bcc}}$  for pure Fe, Cr and Co amounted to -2411 J.mol<sup>-1</sup>, -1281 J.mol<sup>-1</sup> and + 47150 J.mol<sup>-1</sup>, respectively,
- b) using phase boundaries at three temperatures (one of them was the sigma phase apex), the values of  $\Delta H^{\text{sigma} \rightarrow \text{bcc}}$  amounted to -8000 J.mol<sup>-1</sup> (Fe), -9297 J.mol<sup>-1</sup> (Cr from the Fe-Cr data), -6488 J.mol<sup>-1</sup> (Cr from the Co-Cr), and +5289 J.mol<sup>-1</sup> (Co).

c) using phase boundaries at two temperatures (one of them was again the sigma-phase apex) and employing an independent estimate of  $\Delta S_i^{\text{sigma} \rightarrow \text{bcc}}$  the values of  $\Delta H^{\text{sigma} \rightarrow \text{bcc}}$  for pure Fe, Cr and Co were  $-5888 \text{ J.mol}^{-1}$  (Fe),  $-3422 \text{ J.mol}^{-1}$  (Cr from the Fe-Cr data),  $-3090 \text{ J.mol}^{-1}$  (Cr from the Co-Cr data), and  $-7601 \text{ J.mol}^{-1}$  (Co).

Strongly dispersed results presented above have led to an attempt to overcome the necessity of the knowledge of the lattice stability difference by the formulation of substitutional lattice model in the frame of the CEF, as described in [12].

However, for prediction of phase equilibria in ternary and higher order systems, the knowledge of Gibbs energy in metastable region is important. So, the knowledge of physically based lattice stability differences is vital, as it was mentioned above. Here first-principles electronic structure calculations may provide reliable values of total energies, which may be used in construction of complicated phase diagrams.

## 2. First principles calculations of lattice stability

In our recent work [13,14], the total energy calculations of sigma phase and of standard element reference phase (SER) (bcc, hcp) were performed by the Full Potential Augmented Plane Wave (FLAPW) method [15]. This method is based on the density functional theory and uses the full crystal potential. For exchange and correlation energy, we employed the generalized gradient approximation. The unit cell is divided into non-overlapping (muffin-tin) spheres region and interstitial region (plane waves description in the interstitial space is augmented by an atomic-like functions in muffin-tin spheres). The results for optimised total energy difference (relaxed in shape and volume) of sigma phase and SER phase calculated with optimal number of k-points for the Fe, Co and Cr are as follows:

	SER	$\Delta E^{\text{sigma} \rightarrow \text{bcc}} / \text{J.mol}^{-1}$
Co	HCP	-30985
Cr	BCC	-30070
Fe	BCC	-43330

These lattice stability differences enable us to use full physical information about total energy of intermetallic phase and to propose a new model [16] for its thermodynamic description.

This model is based on the two-sublattice model as for solid solution phases (eq.(1)), but the lattice stability difference for the pure constituents (end-members):

$${}^{\circ}G_i^f = {}^{\circ}G_i^{SER} + \Delta^{\circ}E^{SER \rightarrow \sigma} - \Delta S_i^{SER \rightarrow \sigma} T \quad (3)$$

in the metastable or unstable structure is obtained from the results of first-principles electronic structure calculations. ( $\Delta^{\circ}E^{SER \rightarrow \sigma}$ ) mentioned above. This procedure gives physical meaning to energetic parameters of mathematical expression for Gibbs energy difference between the energy of hypothetical structure of end-members and Gibbs energy of its SER state, but the entropy term ( $\Delta S_i^{SER \rightarrow \sigma}$ ) must be adjusted to the phase equilibrium data [8-11]. The results of adjustment are as follows [13,14]:

	$\Delta S^{\sigma \rightarrow bcc} / J.K^{-1}.mol^{-1}$
Co	-0.75
Cr	-0.70
Fe	-0.70

Here thermodynamic parameters for other phases in those systems were taken from the literature [17,18]. In addition, the Redlich – Kister polynomial coefficients L

$$G_{i,j}^{E,\sigma} = y_i y_j (L^0(T) + L^1(T)(y_i - y_j) + \dots) \quad (4)$$

were adjusted to phase equilibrium data [8-11] with following results:

	Fe-Cr	Co-Cr
$L^0$	-133 950	-115 950
$L^1$	31 000	10 800
$L^2$	-127 000	-95 000

Phase diagrams with intermetallic sigma phase of Fe-Cr and Co-Cr systems described by proposed model, have been presented as an example in [13,14] in very good agreement with experimental phase equilibrium data [8-11]. We show those results in Figs. 1a and 1b.

It may be concluded that using ab-initio results characterizing lattice stability of various structures in pure constituents lead to essential improvement of construction of phase diagrams. This approach has a solid physical background and enables us to predict the region of stability of sigma-phase in metallic materials with a better accuracy.

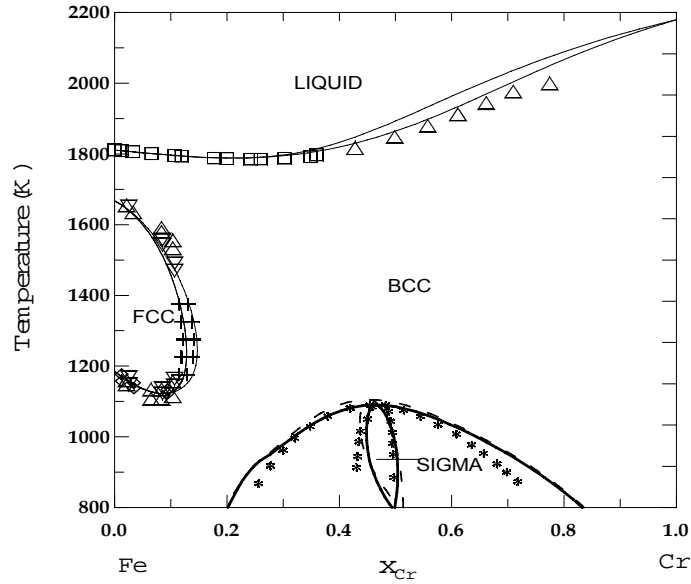


Fig.1a. Phase diagram Cr-Fe. Full lines new model, dotted lines CEF -model.

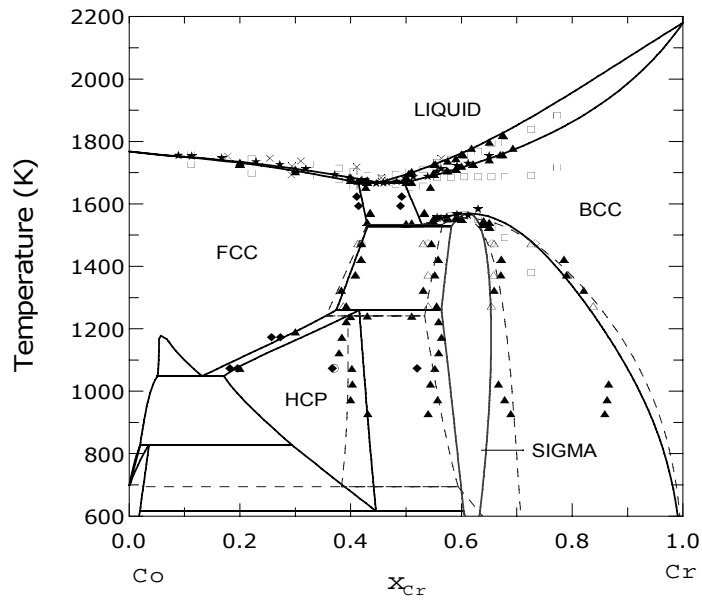


Fig.1b. Phase diagram Co-Cr. Full lines new model, dotted lines CEF - model

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