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**RECENT PROGRESS IN MODELLING OF SIGMA-PHASE****NAJNOWSZE OSIĄGNIĘCIA W MODELOWANIU FAZY SIGMA**

The development of models of intermetallic sigma-phase for calculation of phase diagram is discussed. The physical model of sigma-phase is proposed and tested on the Fe-Cr system. The model is based on the two sublattice model as for solid solution phase, but the structure energy difference for end-members ( $\Delta E_{\text{tot},i}^{\text{sigma-SER}}$ ) is based on the results of calculations of electronic structure from the first principles (Full Potential Linear Augmented Plane Wave – FLAPW – method). Therefore, the energetic parameters of the model have definite physical meaning. Entropy part of Gibbs energy of elements in sigma-phase structure and excess Gibbs energy of mixing of sigma-phase have to be still adjusted to phase equilibrium data. The model could be extended to other complex intermetallic phases.

Omówiono rozwój metod modelowania fazy międzymetalicznej sigma ukierunkowanych na obliczenia wykresu fazowego. Zaproponowano fizyczny model fazy sigma i przetestowano go na przykładzie układu Fe-Cr. Zaproponowany model oparty został na opisie faz stałych „two-sublattice model”, a wartości różnicy energii  $\Delta E_{\text{tot},i}^{\text{sigma-SER}}$  oparte są o wyniki obliczeń struktury elektronowej bazujących na „first principles method” (Full Potential Linear Augmented Wave – FLAPW method). Tym samym, parametry energetyczne modelu posiadają określony sens fizyczny. Człon entropowy energii Gibbsa składników fazy sigma, jak również reszkowa energia Gibbsa mieszania dla tej fazy nadal pozostają dobieralne w oparciu o dane równowag fazowych. Zastosowanie zaproponowanego modelu może zostać rozszerzone do innych złożonych faz międzymetalicznych.

## 1. Introduction

Phase equilibria calculations performed by CALPHAD method (CALculation of PHase Diagrams) are based on a description of thermodynamic properties of phases by means of mathematical expressions (models) which are usually low-order polynomials in the temperature  $T$ , concentrations  $x$  (molar fraction), etc. For systems in which the free energy varies slowly with these variables, the CALPHAD method gives reliable results [1]. On the other hand, in systems with strongly interacting species, some difficulties arise. It follows, that no general model exists, which could be able to describe thermodynamic properties of phases exhibiting different thermodynamic behaviour, e.g., substitutional solid solutions and line compounds.

Sigma-phase (5 inequivalent lattice sites, 30 atoms per repeat cell) is an intermetallic phase with a large concentration range of stability, similarly as do solutions. In the Fe-Cr system, a sigma-phase was first described by Bain [2] and the phase equilibria with bcc-phase were determined by Cook and Jones [3]. Recently, Willars et.al. [4] has reported 110 intermetallic phases with sigma-phase structure.

For the modelling in the framework of CALPHAD method, it is necessary to know the structure energy difference between standard Gibbs energy of the concerned phase (which is for any pure component hypothetical) and Gibbs energy of its stable element reference state (SER) for every element involved.

## 2. Sigma-phase as a bcc-based structure

The first attempt to calculate the phase diagram with sigma-phase in Fe-Cr system was made by Kaufman and Nesor [5]. They consider the sigma-phase as a bcc base stoichiometric compound with  $\Delta H^E = 4867 \text{ Jmol}^{-1}$  and  $\Delta S^E = 7.097 \text{ Jmol}^{-1}\text{K}^{-1}$  for  $x_{\text{Fe}} = 0.53$ . Later on, Müller and Kubaschewski [6] calculated the phase diagram of Fe-Cr on the basis of critically evaluated thermodynamic properties of phases with  $\Delta G^E$  expressed from experimentally determined  $\Delta H^E$  (4749–5104  $\text{J.mol}^{-1}$ ) and  $\Delta S^E$  (1.4815–1.7745  $\text{J.mol}^{-1}\text{K}^{-1}$ ) for  $x_{\text{Fe}}$  [0.49–0.57]. In both cases the bcc structure was regarded as a standard state for sigma-phase. This approach ignored the real structure of sigma-phase and, therefore, the attempts to determine the structure energy difference between Gibbs energy of sigma-phase and that of SER-phase have started.

## 3. Lattice stability of sigma-phase

An estimation of the lattice stability of sigma-phase was performed by Allibert et.al. [7], by extrapolating the experimental values of thermodynamic properties from relatively narrow solution region into the pure components (end-members). This should give a reasonable structure energy difference value.

The structure energy difference listed in their paper was:

$$\text{Fe: } {}^0G^{\text{sigma}} - {}^0G^{\text{bcc}} = 4603.28 + 0.22259 \cdot T$$

$$\text{Cr: } {}^0G^{\text{sigma}} - {}^0G^{\text{bcc}} = 2509.77 + 3.23 \cdot T$$

The results of extrapolations differed one from another, depending on the systems containing the chosen pure component. Thus, the results had to be averaged and such extrapolation over a great deal of phase diagrams is again questionable.

#### 4. Sublattice model of sigma-phase

To overcome this difficulty, the sublattice model for sigma-phase was proposed by Anderson and Sundman [8], which creates the expression for standard Gibbs energy of sigma-phase. Starting from the detected structure of sigma-phase with 5 inequivalent lattice sites, this model compares their Gibbs energy with the standard Gibbs energy of real structures of pure metals in question. This empirical model of standard Gibbs energy of sigma-phase contains adjustable parameters, which are determined by fit to all available experimental data. This procedure was summarised in Ringberg workshop 1996 in the guidelines for reducing the number of sublattices in modelling intermetallic phases by the Compound Energy Formalism (CEF) [19] as follows:

- combine all sublattices with the same coordination number (CN) and similar point symmetry into one,
- if more than two remain, combine the two with highest CN into one,
- arrange the reduced set of sublattices in the order of increasing CN,
- *B* elements will go preferentially into the first sublattice but it may dissolve also some *A* ones,
- the next sublattice will be preferentially filled with *A* elements but may also dissolve some *B* ones,
- if there is a third sublattice, it will be reserved for *A* elements.

Elements of the first transition series and Mo are classified by Kasper [10–12] in two groups: elements to the right of Mn (i.e., Fe, Co Ni) are grouped together and called *B*, while those to the left (i.e., V, Cr, Mo) are designated *A*. manganese appeared to be considered in both groups. Positions with icosahedral surroundings (i.e., CN = 12) tend to be occupied by *B* elements; sites of highest CN (15 and 16) by *A* elements, and statistical distribution may occur in positions with an intermediate CN (13 and 14).

As an example, the following formula for sigma-phase was obtained  $B_8(A,B)_{18}A_4$  [8] or later  $(A,B)_{10}(A,B)_{16}A_4$  [9].

The values of Gibbs energy parameters for 8:18:4 model sigma-phase in Fe-Cr system results as follows:

$${}^0G^{\text{sigma}}_{\text{Fe:Cr:Cr}} = 8 \cdot {}^0G^{\text{FCC}}_{\text{Fe}} + 22 \cdot {}^0G^{\text{BCC}}_{\text{Cr}} + 49000. - 31.0 \cdot T;$$

$${}^0G^{\text{sigma}}_{\text{Fe:Cr:Fe}} = 8 \cdot {}^0G^{\text{FCC}}_{\text{Fe}} + 4 \cdot {}^0G^{\text{BCC}}_{\text{Cr}} + 18 \cdot {}^0G^{\text{BCC}}_{\text{Fe}} + 72000. - 31.0 \cdot T.$$

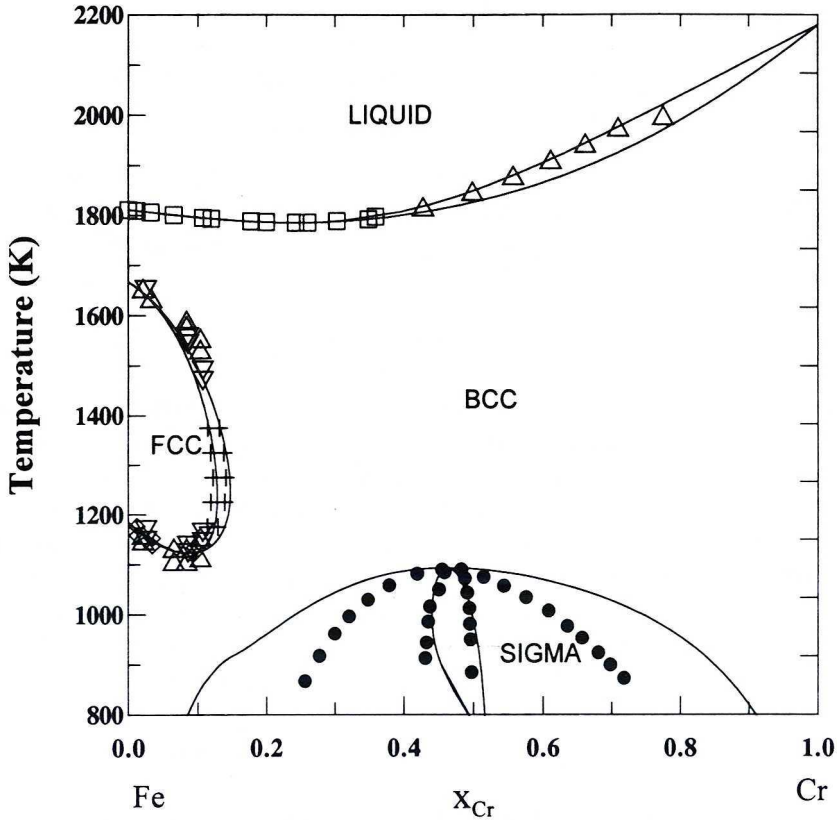


Fig. 1. Calculated phase diagram of Fe-Cr system according to the sublattice model of sigma-phase, compared with experimental values of various authors: • - Cook and Jones [3],  $\Delta$  - Adcock [18],  $\square$  - Hellawell and Hume-Rothery [19],  $\diamond$  - Bungardt et al. [20],  $\nabla$  - Baerlecken et al. [21], + - Nishizawa [22]. Thermodynamic data for liquid, fcc and bcc phases were taken from [13]

Other thermodynamic data were taken from [13]. The above values were adjusted to the phase equilibrium data and, as can be seen in the Fig. 1. As an example, the agreement of calculated phase equilibrium data with experimental ones was achieved for Fe-Cr system. The values of Gibbs energies of phases at 1000 K are shown in Fig. 2. It needs to be mentioned that physical background of the proposed procedure of modelling is not fully exact but "it has been defined by convenience" [8]. It only enables to approximate the lattice stability of metastable phase of pure component by means of linear combination of the known stable phase Gibbs energy of pure components (elements) with the same coordination numbers. This makes it possible to express Gibbs energy of standard state of sigma-phase, but this Gibbs energy has to be adjusted to phase equilibrium data of a composition far away from the pure end-member one and, therefore, its physical reliability is again questionable. Both, the energy and the entropy, has to be adjusted in unknown ratio. It is also no longer possible, within this model, to find the value of the thermodynamic function  $G$  for a composition corresponding to either pure A or pure

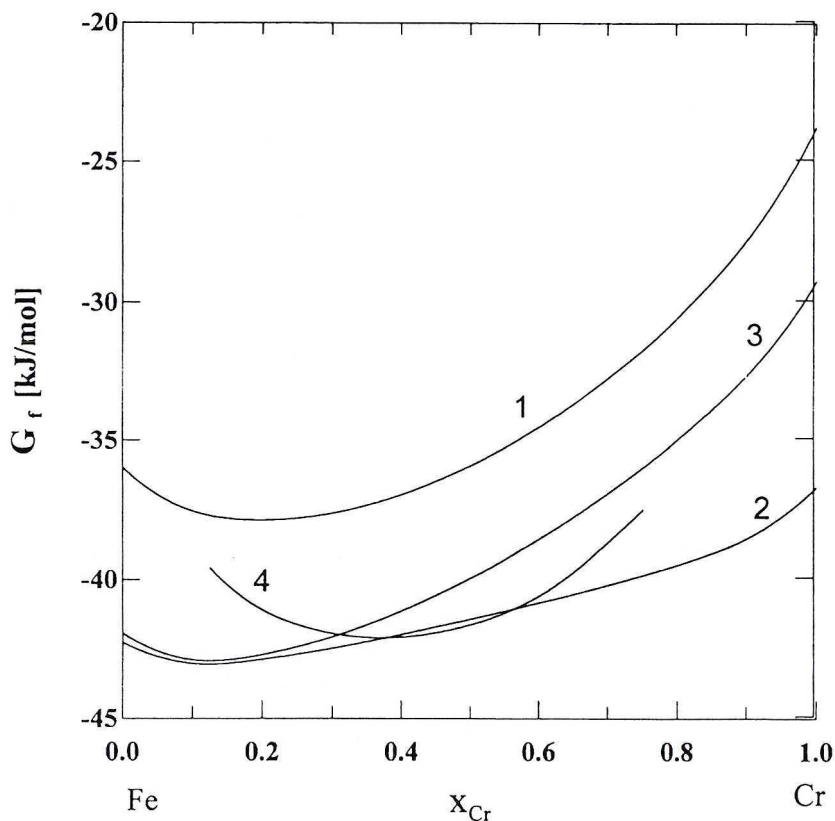


Fig. 2. Gibbs energy of phases in the Fe-Cr system at 1000 K according to the sublattice model of sigma-phase: 1 – liquid, 2 – bcc, 3 – fcc, 4 – sigma

B. Further, it is known from X-ray studies [4], that the mixing of components takes place to some extent in all sublattices, what is not respected by the proposed model [9].

One of the most significant shortcomings of the CEF is the restriction of the entropy of mixing to that of an ideally random mixture. This assumption is contained also in the paper of Pratt and Jones [14], who used pair-wise interaction model for the description of the sigma-phase. By the restriction to randomness, the short range order (SRO) is ignored and a part of the contribution of SRO to Gibbs energy is hidden in the “excess term” after the adjustment of parameters to experimental data. Better description of SRO can be achieved by Cluster Variation Method (CVM) of configurational entropy and by Cluster Expansion Method (CEM) of the mixing energy. The application of mentioned methods in CALPHAD treatment is promising, but not yet commonly used.

Further it is necessary to take into account, that the metastable structures can be completely unstable. This is the case, e.g., for fcc Cr, fcc Fe and bcc Co which follows from the calculation of total energy from the first-principles along trigonal or tetragonal deformation path [15]. In the case of unstable structures the instability with respect to some vibrational mode has the consequence, that the entropy and therefore also Gibbs energy is not exactly defined. To the best of our knowledge, it is not known whether sigma-phase structure is metastable or unstable, so the entropy value must be preliminary regarded as “effective”.

## 5. Physical model of sigma-phase

The use of ab initio computations of the total energies of complex phases had been extended recently. The structure energy difference, calculated by FLAPW (Full potential augmented plane wave) method enables us to use full physical information about sigma-phase (based on X-ray results) and to re-use the older model [7] for its thermodynamic description. Knowledge of the correct value of total energy difference between sigma phase and SER state phase of end-members from first-principles calculation makes it possible to build the Gibbs energy difference of pure components (lattice stability) on physically correct energetic base. The entropic term has to be adjusted to phase equilibrium data only.

The Gibbs energy values for real sigma-phase alloy could be calculated for continuously varying composition of sigma-phase by interpolation of the results of total energy calculations performed for discrete compositions. But the interaction parameters  $L$ , necessary for  $G^{E,\text{sigma}}$  description, have to be adjusted to phase equilibrium data.

Finally, the proposed model is based again on the two sublattice model, similarly as for solid solution phase, but as mentioned above the structure energy difference for end-members ( $\Delta E_{\text{tot},i}^{\text{sigma-SER}}$ ) is based on the results of calculations of electronic structure from the first-principles mentioned above. The Gibbs energy of the sigma-phase may be then expressed by means of the relation:

$$G_m^{\text{sigma}} = \sum_i x_i {}^0G_i^{\text{sigma}} - TS_m^{\text{ideal}} + G^E \quad (1)$$

where

$${}^0G_i^{\text{sigma}} = {}^0G_i^{\text{SER}} + \Delta E_{\text{tot},i}^{\text{sigma-SER}} - TS_i^{\text{vib,sigma}} \quad (2)$$

$$S_m^{\text{ideal}} = -R \sum_i (x_i \ln x_i) \quad (3)$$

$$G^E = x_i x_j ({}^0L_{i,j}^{\text{sigma}} + {}^1L_{i,j}^{\text{sigma}} (x_i - x_j)) \quad (4)$$

This procedure gives a physical meaning to parameters of the mathematical expression for Gibbs energy difference between the energy of a hypothetical sigma-phase structure of end-members and of the Gibbs energy of its standard element reference state. So, the knowledge of the total energy difference between pure elements in the sigma phase structure and in other relevant structures gained by ab initio calculations could substantially simplify the physical modeling of the thermodynamic properties of the sigma phase (and other relevant intermetallic phases) in the CALPHAD method. Thermodynamic properties get correct physical background. Preliminary results of total energy calculation (based on the calculations at experimental volume – calculations at equilibrium volume are in progress) lead to the evaluation of the total energy difference between sigma-phase and SER-phase at 0 K [16]:

$$\Delta E_{\text{tot,Fe}}^{\text{sigma-SER}} = 40300 \text{ J.mol}^{-1}$$

$$\Delta E_{\text{tot,Cr}}^{\text{sigma-SER}} = 20300 \text{ J.mol}^{-1}$$

The value of  $S_i^{\text{vib}}$  has to be adjusted to phase equilibrium data only, supposing a metastable sigma-phase structure. In the case of an unstable structure the value of  $S_i^{\text{vib}}$  adjusted to experimental phase data could be regarded as “effective” value. The best way we propose for the unification of  $S_i^{\text{vib, sigma}}$  gained by optimisation of various systems is to start with the prototype sigma-FeCr, and further to optimise stepwise entropy term by means of  $\Delta E_{\text{tot}, i}^{\text{sigma-SER}}$  for other elements  $i$ . In such a procedure it is necessary to optimise entropy term for only one element  $i$  in every new binary system.

The value of  $G^E$  could than be expressed by a polynomial (e.g., Redlich-Kister – eq. (4)), taking into account SRO. First-principles calculations at 0 K yield the concentration dependence of  $E_{\text{tot}}$  for sigma-phase in various systems. Such results could be found, e.g., in [16] and [17] – made within a simpler Linear Muffin-Tin Orbital Method in Atomic Sphere Approximation (LMTO-ASA) – and could be used as a starting guess for the adjustment to phase equilibrium data. It needs to be mentioned that the  $G^E$  in eq. (1) consists of  $E_{\text{tot}}(x)$  and of the products T.S., where S contains both

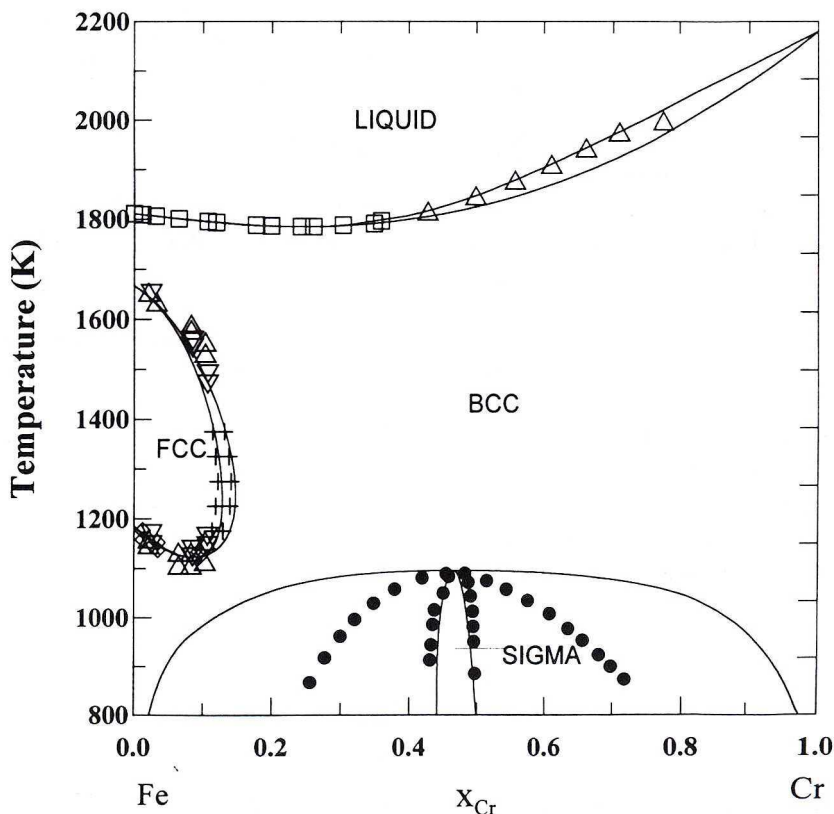


Fig. 3. Calculated phase diagram of Fe-Cr system according to the physical model of sigma-phase, compared with experimental values of various authors: • – Cook and Jones [3],  $\Delta$  – Adcock [18],  $\square$  – Hellawell and Hume-Rothery [19],  $\diamond$  – Bungardt et al. [20],  $\nabla$  – Baerlecken et al. [21], + – Nishizawa [22]. Thermodynamic data for liquid, fcc and bcc phases were taken from [13]

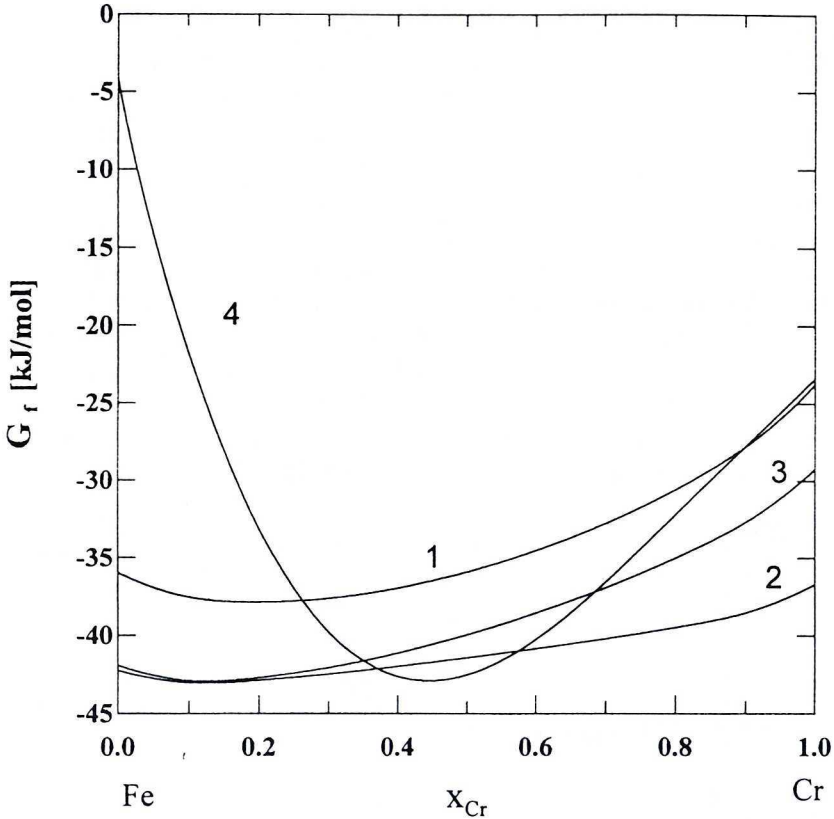


Fig. 4. Gibbs energy of phases in the Fe-Cr system at 1000 K according to the physical model of sigma-phase: 1 - liquid, 2 - bcc, 3 - fcc, 4 - sigma

entropy of configuration and of vibration of the sigma phase alloy. To test the preliminary total energy calculations results by phase diagram calculation the values of thermodynamic functions were taken from [13] for Fe-Cr system. Actual values of Gibbs energy differences for sigma-phase structure of elements and values of excess Gibbs energy parameters (see eq. (4)) are given below.

$$\text{Fe: } {}^{\circ}G^{\text{sigma}} - {}^{\circ}G^{\text{bcc}} = +40300.-3.\text{*T};$$

$$\text{Cr: } {}^{\circ}G^{\text{sigma}} - {}^{\circ}G^{\text{bcc}} = +20300.-7.\text{*T};$$

$${}^{\circ}L^{\text{sigma}}_{\text{Cr,Fe}} = -159000.+67.\text{*T};$$

$${}^1L^{\text{sigma}}_{\text{Cr,Fe}} = 65000.;$$

Phase diagram calculations using the sigma-phase description in terms of the proposed model and ab initio results yield equally good agreement with experimental data as the sublattice model. It is shown for Fe-Cr system as an example in Fig. 3. Thermodynamic functions described for Fe-Cr system by proposed model are shown in Fig. 4. Extension to the ternary system Fe-Cr-Co has been tested also successfully.



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## REFERENCES

- [1] G. Grimval, M. Thiessen, A. F. Guillermet, *Phys. Rev.* **B36**, 7816–7826 (1987).
- [2] E.C. Bain, *Chem. and Met.Eng.* **28**, 23 (1923).
- [3] A.J. Cook, F.W. Jones, *J.Iron Steel Inst.* **148**, 217 (1943).
- [4] P. Villars, L.D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases*, ASM International, Materials Park, Ohio, USA, 1991.
- [5] L. Kaufman, H. Nesor, *Z. Metallkde.* **64**, 249 (1973).
- [6] F. Müller, O. Kubaschewski, *High Temp., High Press.* **1**, 543 (1969).
- [7] C. Allibert, C. Bernard, G. Effenberg, H.-D. Nüssler, P.J. Spencer, *Calphad* **5**, 227–237 (1981).
- [8] J.-O. Anderson, B. Sundman, *Calphad* **11**, 83–92 (1987).
- [9] M. Hillert, *Calphad* **22**, 127–133 (1998).
- [10] I. Ansara et al., *Calphad* **21**, 171–218 (1997).
- [11] J.S. Kasper, "Atomic and Magnetic Ordering in Transition Metal Structure" in "Theory of Alloy Phases", ASM, Cleveland, OH, 264–278 (1956).
- [12] J.S. Kasper, R.M. Waterstrat, *Acta Cryst.* **9**, 289–295 (1956).
- [13] J. Vřešťál, J. Tomiska, P. Brož, *Ber. Bunsenges. Phys. Chem.* **98**, 1601 (1994).
- [14] J.N. Pratt, L.I. Jones, *Calphad* **8**, 75–91 (1984).
- [15] P.J. Craevich, M. Weinert, J.M. Sanchez, R.E. Watson, *Phys. Rev. Lett.* **72**, 3076–3079 (1994).
- [16] J. Havránková, J. Vřešťál, L. Wang, M. Šob, *Phys. Rev.* **B63**, 174104 (2001).
- [17] M.H.F. Sluiter, K. Esfarjani, Y. Kawazoe, *Phys. Rev. Lett.* **75**, 3142 (1995).
- [18] F. Adcock, *J. Iron Steel Inst.* **124**, 99 (1931).
- [19] A. Hallawell, W. Hume-Rothery, *Phil. Trans. Roy Soc. London* **A-249**, 417 (1957).
- [20] K. Bungardt, E. Kunze, E. Horn, *Arch. Eisenhüttenw.* **29**, 193 (1958).
- [21] E. Baerlecken, W.A. Fischer, K. Lorenz, *Stahl Eisen* **81**, 768 (1961).
- [22] T. Nishizawa, Rep. 4602, Swedish Board of Technical Development, Stockholm 1966.

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