The system Fe–Ni–Cr: revision of the thermodynamic description

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Abstract

The phase diagram of the ternary Fe–Ni–Cr alloys has been reassessed for temperatures higher than 1070 K using substantially more thermodynamic data from experimental investigations than previous attempts. The new thermodynamic description reduces the magnetic contribution terms to the expressions of the pure species only. The calculated phase equilibria yield a distinct improved overall-agreement with the experimental data than the results of previous assessments. The present thermodynamic description reproduces the distribution coefficients better than previous data. Complete lists of the data sets of all binary and ternary parameters, several isothermal and vertical sections as well as various projections are presented.

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1. Introduction

The phase relations of ternary Fe–Ni–Cr alloys have been investigated by many authors because these alloys are of considerable technical and great practical importance: Many corrosion-resistant alloys, e.g. austenitic stainless steels have the Fe-rich corner of the Fe–Ni–Cr system as their compositional base. Critical assessments of the experimental literature on phase equilibria of Fe–Ni–Cr alloys up to the middle of the 1980s has been compiled thoroughly by Rivlin [1] and Raynor and Rivlin [2]. Newer measurements on the tie lines and the liquidus surfaces of the liquid–bcc solid and liquid–fcc solid equilibria in the iron-rich corner of the Gibbs triangle are reported by Kundrat and Elliott [3]. Sopousek and Kruml [4] determined some points of the sigma(e)/fcc solid equilibrium.

Computer synthesis of ternary phase equilibria curves have been performed by several authors until now [3,5–9]. However, these assessments are based upon poor experimental data of the thermodynamic mixing behavior, only. The cited authors employed mainly sets of “Gibbs energy data” which have been obtained by means of “trial and error” techniques. It is not surprising that Hillert and Qiu [8] reported that their own as well as the previous assessments suffered from the same difficulties, especially concerning the distribution coefficients (the isothermal ratio of equilibrium species-concentration in two coexisting phases) of Ni and Cr, $K_{ij}^{(e)}$ ($k = \text{Ni}, \alpha = \text{fcc}$; $k = \text{Cr}, \alpha = \text{bcc}$). These authors concluded that it is not possible to get good agreement between the computed distribution coefficients and the experimental tie lines within the framework of the thermodynamic models and binary descriptions adopted in their work (compare Fig. 1).

Lee [9] reported later, a revision of the thermodynamic data as assessed by Hillert and Qiu [8] especially with respect to the descriptions of the binary Fe–Ni and Cr–Fe alloys that yields a better agreement with the experimental data in the Fe-rich region of the Fe–Ni–Cr ternary system than previous assessments. This is in full agreement with mass spectrometric measurements on Fe–Ni and Cr–Fe alloys as published earlier [10–12]. Nevertheless, the full experimental Fe–Ni data available at that time was not considered, not even in the revision by Lee [9].

In the last years mass spectrometric investigations have yielded the thermodynamic mixing behavior of binary bcc solid Ni–Cr [13] alloys, as well as ternary liquid [14] and fcc solid [15] Fe–Ni–Cr alloys. Furthermore, it has been shown in [16] that the liquidus/solidus and bcc/fcc phase equilibria in the Fe–Ni system can be computed in full agreement with the experimental data without any binary
magnetic correction term as used by Hillert and Qiu [8] and Lee [9]. As an illustration in Fig. 2 the liquidus-fcc phase boundary as obtained in [16] is compared with the corresponding phase boundaries as reported by Hasebe and Nishizawa [6], Hillert and Qiu [8], and Lee [9]. Therefore a re-calculation of the Fe–Ni–Cr phase diagram in the temperature range 1073–1873 K without employing binary or ternary magnetic corrections seemed to be of interest.

2. Computer-aided modeling of Fe–Ni–Cr phase diagram

The computations of phase boundaries are using the thermodynamic equilibrium conditions that at constant temperature \( T \) the partial Gibbs energy \( G_k^\alpha(T,x_k^\alpha) \) (also: "molar chemical potential \( \mu_k^\alpha(T,x_k^\alpha) \)"") for each component \( k \) (this work; \( k = \text{Fe}, \text{Ni}, \text{Cr} \); \( x_k \) are the mole fractions) must be equal in each of the coexisting phases \( \alpha, \beta, \ldots \) = \( l, f, b, s, \ldots \); \( l = \text{liquid}, f = \text{fcc}, b = \text{bcc}, s = \text{sigma} \))

\[
G_k^\alpha(T,x_k^\alpha) = G_k^\beta(T,x_k^\beta) = G_k^l(T,x_k^l) = \ldots
\]

\( k = \text{Fe}, \text{Ni}, \text{Cr} \),

(1)

where \( x_k^\alpha \), \( x_k^\beta \) are the equilibrium compositions in the phases \( \alpha, \beta, \ldots \). Additional advantage of this method is the possibility to synthesize the phase diagrams of real alloys over a wide range of composition and temperature by computation combined with thermodynamic analysis of experimental molar functions \( Z \) (\( Z = \text{Gibbs energy G, heat of mixing H, entropy S} \)).

However, the computational techniques require the explicit values of the molar Gibbs energy \( G \) in all coexisting phases over the whole employed temperature ranges—even at temperatures at which the various phases are not stable any more. Consequently, no phase equilibrium can be computed by means of experimentally determined thermodynamic data only. Data required additionally have to be estimated and/or derived by means of more or less suitable extrapolation techniques. It is obvious from Eq. (1), computational synthesis of phase equilibria curves require only the differences of the molar Gibbs energy \( G \) and not their absolute values. This makes possible not only basically different strategies of assessment, but also the use of many different sets of thermodynamic parameters to describe more or less satisfactorily the Fe–Ni–Cr phase diagram. Concerning details of the various techniques the book of Saunders and Miodownik [17] should be consulted.

After an early modeling by Kaufman and Neser [5] especially Hasebe and Nishizawa [6] succeeded in employing Kaufman’s so-called lattice stability functions for computational establishing of phase equilibria in the ternary Fe–Ni–Cr system which are in reasonable agreement with experimental data. In a first step the phase equilibria in the Fe–Ni–Cr system were examined by microprobe analysis of ternary diffusion couples consisting of their components.
Their experimental data were then analyzed thermodynamically using an extended regular solution model and the thermodynamic data on the binary systems concerned. Linear programming yielded finally the thermodynamic parameters required by the authors for synthesis of the phase diagram over a wide range of temperature.

Chart et al. [7] also used for their assessment the concept of lattice stability functions. These authors generated for theircomputations of the phase relations in the temperature range 650−1000 K a thermodynamic data set distinctly different to that of Hasebe and Nishizawa [6]. The latest assessment employing Kaufman’s lattice stability concept has been performed by Kundrat and Elliott [3]. They reinvestigated the iron-rich corner of the Fe–Ni–Cr system both by measurements as well as by modeling of tie-lines and the liquidus surfaces of the liquid–bcc (8) and liquid–fcc (7) equilibria and the peritectic surface involving all three phases in the iron-rich corner of the Gibbs triangle. The thermodynamic parameters as used in (3.5.7) for the phase diagram calculations based upon lattice stability functions are called in the literature as “Gibbs energy”, although they are basically different to the physical notion of the molar Gibbs energy. Therefore “Gibbs energy” should not be used in context with lattice stability functions any longer. May be a notion like “phase equilibria function” should be introduced instead to characterize apparently that these functions are only employable for phase diagram computations—and not for any other application in alloy thermodynamics.

Hillert and Qiu [8] as well as Lee [9] based their assessments upon modeling the molar Gibbs energy $G^\alpha(T, x^\alpha)$ in a phase $\alpha$ as following (phase index $\alpha$ omitted)

$$G(T, x) = G^\beta(T) + G^\gamma(T, x) + G^\delta(T, x) + G^\phi(T, x), \quad (2)$$

where $G^\beta$ and $G^\delta$ denote the contributions of the pure species, and of the “ideal” alloy, respectively. In Eq. (2) the terms $G^\gamma$ and $G^\phi$ are assumed commonly to be due to the intermolecular and magnetic forces, respectively. These authors assessed the ternary parameters for the liquid, bcc, and fcc phases, and obtained satisfactory agreement with the experimental phase boundary data. Their assessment reproduced the distribution coefficients better than previous phase synthesis, but still unsatisfying as can be seen from Fig. 1.

Lee’s assessment of the thermodynamic data sets for the Fe–Cr and Fe–Ni liquid phase yields a better agreement with experimental data on the bcc/liquid and fcc/liquid tie-lines and liquidus temperatures in the Fe-rich region of the Fe–Ni–Cr ternary system than the previous assessments. But, as can be noticed from Fig. 1, the distribution coefficients due to Lee’s assessment show partly distinct less agreement with the experimentally determined ones than those as reported by Hillert and Qiu [8].

The experimental data as employed in previous assessments consisted mainly of the results of phase equilibria investigations, and only poor measurements on the molar Gibbs energy have been incorporated. Partly the reason may be seen on a lack of thermodynamic measurements,
because in case of multicomponent alloy systems such as the Fe–Ni–Cr ternary system the thermodynamic investigations for the determination of reliable molar Gibbs energy data are very time-wasting, and usually beset with considerable experimental difficulties. Therefore it may be understandable that authors are ignoring the lack of experimental investigations, and produce their own sets of assessed data. But sometimes the lack of incorporated experimental results cannot be explained by this reasoning: e.g., Hillert and Qiu [8] have taken for their assessment of the Fe–Ni–Cr phase diagram the thermodynamic assessment of the binary boundary system Fe–Ni as reported by Xing et al. [18] and not of the results of mass spectrometric measurements as reported in the same year for the liquid phase in [10], and for the fcc solid alloys in [11]. Fig. 2 shows that the synthesis of phase equilibria curves based upon these mass spectrometrically determined molar excess Gibbs energies $G^E$ as reported in [16] will agree even better with experimental data than Lee’s improved assessment of the data as assessed by Xing et al. [18].

The introduction of a magnetic term $G^M$ as expressed in Eq. (2) is a bit problematical, because experimental investigations will only yield the total excess sum ($G^E + G^M$). However, especially the databases offered by the ThermoCalc group are based upon the use of magnetic terms $G^M$ as expressed by Sundman and Agren [19], which from a physico-chemical point of view their description of assumed magnetic influence, $G^M$, looks a bit strange, e.g., polynomials in temperature up to the power 25 (!) are employed (see [19]). Nevertheless, with respect to the efforts of establishing a general data base for the reference states of the elements it is meaningful to employ elementary magnetic contributions.

By means of newer mass spectrometric investigations on bcc solid Fe–Cr alloys by [12] molar excess Gibbs energies $G^E$ have been determined which are distinctly different to the values of the assessments by Anderson and Sundman [20] and Lee [9]. But, as can be seen from Fig. 3c, a better agreement with the experimental phase equilibria data have been obtained by means of computations based upon these experimentally determined data but without any binary magnetic correction, than the in the assessments by Anderson and Sundman [20] and Lee [9] which have used the binary magnetic contributions. The same situation we are faced in the binary Co–Cr system as reported in [21]. Therefore the suspicion raises, that especially at temperatures above the Néel or Curie temperatures the use of a binary magnetic correction will only improve the quality of binary phase diagrams in cases of employing a bit doubtful excess data.

3. Thermodynamic models

The molar properties $Z(T, x)$ (x denotes the dependence on all three mole fractions $x_i$) of an alloy system with $K$ components $k$ (this work: $K = 3$) in the phase $\alpha$ are characterized commonly by means of the contributions made by the alloy constituents $k$, the so-called partial molar properties $Z_k(T, x)$ (phase index $\alpha$ omitted):

$$Z(T, x) = \sum_{k=1}^{K} x_k Z_k(T, x).$$

(3)

Within temperature ranges, in which the logarithms of the partial pressures of all constituents can be assumed to be inverse proportional to $T$, both the enthalpy of mixing as well as the excess entropy result as temperature independent. The temperature dependence of the molar Gibbs energy $G$ is then given by the well-known relation

$$G(T, x) = H(x) - TS(x),$$

(4)

which is equivalent to the assumption of vanishing molar excess heat capacity ($\Delta C_p = 0$), expressed by the rule of Neumann and Kopp, according to which the difference between the heat capacity of an alloy and the heat capacities of the corresponding amounts of the pure species at the same temperature is zero.

With respect to the efforts of establishing a general data base for the reference states of the elements the magnetic correction term of Eq. (2) have not been omitted entirely but they are reduced to their elementary magnetic contributions $G^M_k(T, x)$. In this work the partial molar Gibbs energy $G_k(T, x)$ are composed therefore by

$$G_k(T, x) = G^E_k(T) + G^M_k(T, x)$$

(5)

with ($R$ is the gas constant)

$$G^M_k(T, x) = RT \ln(x_k).$$

(6)

3.1. The $G^E_k(T)$ reference terms

The $G^E_k(T)$ term in Eq. (5) acts as reference level for the partial Gibbs energy only, and has been expressed as polynomials in $T$ for a long time in literature. With respect to establish a general data base for these reference states of the elements, it is meaningful to employ the reference data as developed by SGTE [22] for this purpose

$$G^E_k(T) = C_{1k} + C_{2k} T + C_{3k} T^2 + C_{4k} T^3 + C_{5k} T^4 + C_{6k} T^5 + C_{7k} T^6 + C_{8k} T^7,$$

(7)

where $C_{nk}$ ($n = 1, \ldots, 8$) are specific coefficients for each element. Table I gives the numerical values of the coefficients $C_{nk}$ after [22] as employed in this work.

3.2. The elementary magnetic contributions $G^M_k(T, x)$

The magnetic correction of the molar Gibbs energy of the pure species, $G^M_k(T, x)$ as presented by Sundman and
Table 1
The coefficients $^4C_n$ of the $G_n^r(T)$ reference terms, Eq. (7), of the liquid, bcc solid, and fcc solid phases from SGTE [22].

<table>
<thead>
<tr>
<th>n</th>
<th>Liquid</th>
<th>bcc</th>
<th>fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k = \text{Fe}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1225.7</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
<tr>
<td>2</td>
<td>124.134</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
<tr>
<td>3</td>
<td>122.57</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
<tr>
<td>4</td>
<td>123.543</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
<tr>
<td>5</td>
<td>123.543</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
<tr>
<td>6</td>
<td>123.543</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
<tr>
<td>7</td>
<td>123.543</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
<tr>
<td>8</td>
<td>123.543</td>
<td>298-1811 K</td>
<td>1811-6000 K</td>
</tr>
</tbody>
</table>

| $k = \text{Ni}$ | | | |
| 1 | 3535.93 | 298-1728 K | 1728-6000 K |
| 2 | 114.298 | 298-1728 K | 1728-6000 K |
| 3 | 114.298 | 298-1728 K | 1728-6000 K |
| 4 | 114.298 | 298-1728 K | 1728-6000 K |
| 5 | 114.298 | 298-1728 K | 1728-6000 K |
| 6 | 114.298 | 298-1728 K | 1728-6000 K |
| 7 | 114.298 | 298-1728 K | 1728-6000 K |
| 8 | 114.298 | 298-1728 K | 1728-6000 K |

| $k = \text{Cr}$ | | | |
| 1 | 3535.93 | 298-2180 K | 2180-6000 K |
| 2 | 114.298 | 298-2180 K | 2180-6000 K |
| 3 | 114.298 | 298-2180 K | 2180-6000 K |
| 4 | 114.298 | 298-2180 K | 2180-6000 K |
| 5 | 114.298 | 298-2180 K | 2180-6000 K |
| 6 | 114.298 | 298-2180 K | 2180-6000 K |
| 7 | 114.298 | 298-2180 K | 2180-6000 K |
| 8 | 114.298 | 298-2180 K | 2180-6000 K |

Agrén [19] can be expressed by the simplified representation:

$$G^0_n(T) = RT \ln^4 B_0 + 1/k \left( \frac{T}{T_c} \right),$$ (8)

where $^4B_0$ is the atomic magnetic moment, and $^4T_c$ is the magnetic ordering temperature (Néel or Curie temperature). The numerical values employed in this work are summarized in Table 2. These authors assumed the function $g(T)$ to be of the form $\bar{T}$ (i.e., $^4T_c$):

for $\tau > 1$:

$$g(\tau) = \frac{\tau^{-1} + \tau^{-5} / 315 + \tau^{-25} / 1500}{B_1},$$ (9a)

and

for $\tau \leq 1$:

$$g(\tau) = 1 + B_2 \tau + B_3 (\tau^2 / 6 + \tau^3 / 135 + \tau^{35} / 600) / B_1,$$ (9b)

where $B_1$ to $B_3$ are phase-dependent constants as given in Table 3.

Table 2
The atomic magnetic moments $^4B_0$, and critical magnetic ordering temperature (Néel or Curie temperature) $^4T_c$ of Eq. (8) of Fe, Ni, and Cr from Sundman and Agrén [19].

<table>
<thead>
<tr>
<th>$k$</th>
<th>$^4B_0$ (K)</th>
<th>$^4T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4B_0$</td>
<td>1.410714</td>
<td>2.015306</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1.430854</td>
<td>2.452429</td>
</tr>
<tr>
<td>$B_3$</td>
<td>1.558625</td>
<td>2.342457</td>
</tr>
</tbody>
</table>

Table 3
The constants $B_1$ to $B_3$ of the function $g(\bar{T})$, Eq. (9), from Sundman and Agrén [19].

<table>
<thead>
<tr>
<th>$B_1$</th>
<th>$B_2$</th>
<th>$B_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.410714</td>
<td>2.015306</td>
<td>2.452429</td>
</tr>
</tbody>
</table>
3.3. The TAP series concept of excess quantities

The binary excess functions $^j_k Z^E$ ($j, k$ components) are represented by ($N$ is the number of adjustable parameters $^j_k C_{nk}$) [23]:

\[
^j_k Z^E_{jk}(x_k) = \sum_{n=1}^{N} \frac{^j_k C_{nk} x_n^2}{dx_k},
\]

(10a)

\[
^j_k Z^E_{jk} = \frac{^j_k Z^E}{dx_k},
\]

(10b)

\[
^j_k Z^E_{jk} = \frac{^j_k Z^E}{dx_k} - \frac{x_k}{dx_k} \frac{^j_k Z^E}{dx_k},
\]

(10c)

\[
\frac{^j_k Z^E}{dx_k} = \sum_{n=1}^{N} \frac{^j_k C_{nk} x_n^2}{dx_k} (x_k - x_k),
\]

(10d)

The customary classification of binary alloys with respect to the adjacency of their excess properties may be performed with more clarity: The TAP parameter $^j_k C_{1}$ and $^j_k C_{2}$ characterize the regular and sub-regular solution contributions as pointed out in [23]. Interchange of the components, as well as conversion of the various literature proposals for polynomial representing of $^j_k Z^E(x)$, especially of the frequently used, but distinctly more complicated Redlich–Kister polynomial into the TAP-series and vice versa can be performed easily by means of the algorithm developed, e.g. in [23].

The ternary excess properties $Z^E$ are represented by adding a ternary interaction term $FeNiCr Z^E$ to the simple sum of the three binary interaction terms, $^j_k Z^E$ [23]. The ternary interaction term $FeNiCr Z^E$ is preferably a simple polynomial in all three mole fractions. Concerning the Fe-Ni-Cr system a polynomial of third order in $x$ was sufficient in all three (bcc, fcc and liquid) phases. The molar excess quantities of Fe–Ni–Cr alloys are represented therefore by Eq. (11) ($1 = Fe$, $2 = Ni$, $3 = Cr$, $^1_2 C^E$ is the ternary adjustable parameter):

\[
Z^E = \frac{^1_2 C^E x_1 x_2 x_3}{dx_3} + \frac{N}{3} \frac{x_1 x_2 x_3}{dx_3} + \frac{x_1 x_2 x_3}{dx_3} \sum_{n=1}^{N} \frac{^1_2 C_{nk} x_n^2}{dx_3},
\]

(11a)

\[
Z^E = Z^E + \frac{x_2 Z^E}{dx_3} - \frac{x_1 Z^E}{dx_3},
\]

(11b)

\[
Z^E = Z^E + \frac{\frac{1}{2} (x_2 x_3 Z^E)}{dx_3} - \frac{x_1 Z^E}{dx_3},
\]

(11c)

\[
Z^E = Z^E + \frac{x_2 Z^E}{dx_3} - \frac{x_1 Z^E}{dx_3},
\]

(11d)

\[
\frac{\partial Z^E}{\partial x_2} = \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_2} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_2} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_2} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_2},
\]

(11e)

\[
\frac{\partial Z^E}{\partial x_3} = \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3},
\]

(11f)

In accordance with Eq. (4), the TAP parameters of the molar excess Gibbs energy $G^E$, of the molar heat of mixing $H^E$, and of the molar excess entropy $S^E$ are connected by

\[
\frac{\partial G^E}{\partial x_3} = \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3},
\]

(12a)

\[
\frac{\partial C^E}{\partial x_3} = \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3} + \frac{1.2 C^E x_2 (x_1 - x_2)}{dx_3},
\]

(12b)

As carried out in [16] the TAP series concept reduces considerably the computational effort. Conversion of the TAP series into other polynomial representations (e.g. Redlich–Kister expansions as employed in [8,9]), and vice versa, can be performed easily by means of the algorithm presented in [23].

3.4. Modeling of the $\sigma$-phase

Considering the $\sigma$-phase of the investigated temperature range in literature no experimental thermodynamic data are available. Therefore the adjustment to phase equilibrium data has been performed using the sublattice model of solid phases according to Anderson and Sundman [20]. The atoms in different sublattices are compared with the atoms in the bcc or fcc structures. Formally, three sublattices are considered [20]: The first occupied by 8 atoms is compared with fcc lattice and the other two occupied by 4 and 18 atoms, respectively, with the bcc lattice. In third sublattice both iron and chromium atoms can be present. Standard Gibbs energy is equal to

\[
G^E_{FeCr} = 8G^E_{Fe} + 4G^E_{Cr} + 18G^E_{bcc},
\]

(13a)

\[
G^E_{FeNi} = 8G^E_{Fe} + 4G^E_{Ni} + 18G^E_{bcc},
\]

(13b)

\[
G^E_{FeNiCr} = 8G^E_{Fe} + 4G^E_{Ni} + 18G^E_{Cr},
\]

(13c)

For $\sigma$-phase containing nickel we suppose, that nickel can be present in the first sublattice with iron and in the third sublattice with iron and chromium:

\[
G^E_{FeCrNi} = 8G^E_{Fe} + 4G^E_{Cr} + 18G^E_{Ni},
\]

(13d)
Table 4
The $C_T^a$ and $C_T^{b,c}$ parameters of Eq. (12) for the molar Gibbs energy of $\sigma$-phase as fitted in this work.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$C_T^a$ ($\text{J mol}^{-1}$)</th>
<th>$C_T^{b,c}$ ($\text{J mol}^{-1}$ K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>49000</td>
<td>−31</td>
</tr>
<tr>
<td>2</td>
<td>72000</td>
<td>−31</td>
</tr>
<tr>
<td>3</td>
<td>187000</td>
<td>−200</td>
</tr>
<tr>
<td>4</td>
<td>305000</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ G^a_{\text{FeCrNi}} = 8C_T^{b,c} + 4C_T^{b,c} \text{Cr} + 18C_T^{b,c} \text{Fe} + (C_T^a + C_T^{b,c} T). \]  

The superscript bcc denotes a hypothetical paramagnetic bcc-phase. The numerical values of the parameters $C_T^{b,c}$ and $C_T^a$ for the molar Gibbs energy of $\sigma$-phase, Eq. (13), as fitted in this work are presented in Table 4.

4. Thermodynamics

Following the SGTE [22] the latest values for the melting temperatures of Fe, Ni, and Cr are: $T_m^{\text{Fe}} = 1811$ K (instead of 1808 or 1809 K), $T_m^{\text{Ni}} = 1728$ K (instead of 1725–1726 K), and $T_m^{\text{Cr}} = 2180$ K (instead of 2123–2151 K). These data have been used first by the assessments of Hillert and Qu [8] and Lee [9]. The synthesis of the phase relations of this work is also based upon these melting points of the three constituents. In [12] the experimental phase diagram data of Cr–Fe at temperatures higher than the melting point of Fe have been raised proportional to the old and new differences of the melting points of the constituents, therefore. This causes some discrepancies to the figures as presented in the original literature.

We cannot expect that experimental data of the thermodynamic mixing behavior yield directly satisfactory phase boundaries, as our techniques of experimental investigations are not precise enough for this purpose. However, assessments within the accuracy limits of 5–20% of the parameter values of trusted experimental investigations should yield reasonable results, and unrealistic behavior of the thermodynamic activities avoided. The phase relations as presented in this work have been obtained by means of minor optimizations of about 5% of the original mass spectrometric data.

4.1. The binary systems Fe–Ni, Ni–Cr, and Cr–Fe

The TAP parameters $\Delta C_v$ of the molar excess properties $\Delta$ (Z = G, H, S) of the three binary boundary systems Fe–Ni, Ni–Cr, and Cr–Fe as used in this work are given in Tables 5–7. The resultant phase equilibria curves are presented in Fig. 3. As carried out in [16] slight modifications (up to 5%) of the results of mass spectrometric measurements both on the liquid [10] and for the solid [11] phase makes possible to determine Fe–Ni phase equilibria curves without involving any binary magnetic correction term. As Fig. 3a makes evident, the liquidus/solidus phase equilibria of Fe–Ni based upon the simpler thermodynamic modeling as suggested in [16] yield full agreement with both the experimental phase equilibria data as well as with the results of the assessment of Hasebe and Nishizawa [6]. The peritectic temperature (1796 K) is in accordance with the experimentally determined data of Hellawell and Hume-Rothery [25] and Schirmann et al. [26] as well as with the critical experimental assessment of Rivlin [1], and with the computations of Hasebe and Nishizawa [6]. Whereas Lee’s assessment yielded a peritectic temperature of 1791 K. The assessment of the thermodynamic excess behavior of the bcc solid phase has been based in [16] on the mass spectrometrically determined data of the liquid and the bcc solid phases. As carried out in detail in [16], the resultant bcc/liquid and bcc/fcc phase equilibria lines are in good agreement with the experimental information. In Fig. 4 the experimental points of the low temperature bcc/fcc

Table 5
TAP parameters $^{\text{Ni,Ni}}C_T^a$ of Fe–Ni alloys ($C_T^a = C_T^a - TC_T^a$) from [16]

<table>
<thead>
<tr>
<th>$n$</th>
<th>Liquid</th>
<th>bcc</th>
<th>fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_T^a$ (J mol$^{-1}$)</td>
<td>$C_T^a$ (J mol$^{-1}$ K)</td>
<td>$C_T^a$ (J mol$^{-1}$)</td>
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<tr>
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<td>−10500</td>
<td>−1.85</td>
<td>−2400</td>
</tr>
<tr>
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</tr>
<tr>
<td>3</td>
<td>−6000</td>
<td>−5.05</td>
<td>−12000</td>
</tr>
</tbody>
</table>

Table 6
TAP parameters $^{\text{Ni,Cr}}C_T^a$ of Ni–Cr alloys ($C_T^a = C_T^a - TC_T^a$)

<table>
<thead>
<tr>
<th>$n$</th>
<th>Liquid</th>
<th>bcc</th>
<th>fcc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$C_T^a$ (J mol$^{-1}$)</td>
<td>$C_T^a$ (J mol$^{-1}$ K)</td>
<td>$C_T^a$ (J mol$^{-1}$)</td>
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<tr>
<td>2</td>
<td>5400</td>
<td>9</td>
<td>44610</td>
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</table>

Liquid and fcc phase optimized in [24] (all data converted into TAP series concept), bcc phase from [13].
As reported in [13] the phase diagram shown in Fig. 3b agrees also well with the assessed Ni–Cr diagram reported by Nash [29]. The fcc–bcc equilibrium calculated by Chuang and Chang [30] coincides also with the results plotted in Fig. 3b, whereas the computations of these authors yielded fcc–liquid and liquid–bcc equilibria which show less agreement with the experimental data than the phase equilibrium curves based upon the TAP parameters given in Table 6.

A detailed discussion of the experimental studies of binary Cr–Fe alloys is given in [12]. Based upon their own experimental data of the excess properties, in [12] the thermodynamic descriptions of the liquid, the fcc solid, and the sigma phase have been re-optimized by means of computational phase equilibrium synthesis. The assessment as reported in [12] yielded a description of the solidus–liquidus equilibrium of Fe–Cr alloys showing better agreement with the experimental phase equilibrium data than the earlier optimizations.

The synthesis in [12] still used magnetic correction terms, and it seemed to these authors that the magnetic contribution should be essentially for describing the phase regions of solid Fe–Cr alloys. However the computations in this work showed that the binary magnetic correction can be omitted by simple raising the assessed TAP parameter $C_{FeCr}^{m}$ of the heat of mixing of the fcc solid phase about 4%. This slight correction makes it already unnecessary to employ a binary magnetic correction. The corresponding TAP parameters are summarized in Table 7. Consequently the thermodynamic characterization of the $\sigma$-phase have been reassessed in this work, too. The new data are given in Table 4 ($C_{FeCr}^{m}$ and $C_{FeCr}^{m}$; $n = 1$, 2). The resultant phase equilibrium curves are plotted together with the experimental phase diagram data in Fig. 3c.

### 4.2. Ternary Fe–Ni–Cr alloys

The ternary interaction TAP parameters $FeNiCr C^{2}$ of the molar excess quantities properties $Z$ ($Z = G, H, S$) of ternary Fe–Ni–Cr alloys as used in this work are summarized in Table 8. The resultant phase equilibrium curves are

<table>
<thead>
<tr>
<th>$n$</th>
<th>$C_{Cr}^{2}$ (J/mol)</th>
<th>$C_{Cr}^{2}$ (J/mol)</th>
<th>$C_{Cr}^{2}$ (J/mol)</th>
<th>$C_{Cr}^{2}$ (J/mol)</th>
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<td>-4500</td>
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</table>

**Table 7**

<table>
<thead>
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<th>$n$</th>
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<th>bcc</th>
<th>fcc</th>
</tr>
</thead>
<tbody>
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<td>-3100</td>
</tr>
<tr>
<td>2</td>
<td>-3000</td>
<td>0</td>
<td>-4400</td>
</tr>
</tbody>
</table>

**Table 8**

The fcc phase optimized in this work from phase diagram calculations; liquid and bcc phase from [12].
presented in Figs. 5–8. The mass spectrometric investigations from [14] yielded the first experimental data for the thermodynamic mixing behavior of the liquid Fe–Ni–Cr alloys over the whole range of ternary compositions. The molar excess properties of fcc solid Fe–Ni–Cr alloys have been determined mass spectrometrically by [15]. In both cases using one adjustable ternary interaction term is sufficient, but really necessary, for a satisfying description of experimental molar excess properties. Whereas the assessments by Hillert and Qiu [8] and Lee [9] employed three ternary terms for this purpose in the fcc solid phase. For discussion of the poor earlier experimental studies see [14, 15].

Concerning the bcc and the σ-phases no experimental molar excess properties have been available, the thermodynamic description of these two phases has been re-assessed in this work by means of the computational phase equilibria synthesis using the molar mixing behavior of the liquid and fcc solid phases from [14, 15]. Again only one temperature dependent ternary interaction term was necessary—in contrast to the previous assessments of by Hillert and Qiu [8] and Lee [9] which required two ternary interaction terms. The resultant ternary TAP parameters FeNiCrCeCe of the bcc phase are presented in Table 8. The new values of the adjustable coefficients for the description of the σ-phases (C0 1, 1 and C0 1, 2: n = 3, 4) are summarized in Table 4.

5. Results and discussion

Fig. 5 shows selected isothermal sections involving the liquid phase from 1873 K down to 1625 K. In Fig. 6 the temperature development is presented as obtained in this work for the liquid/bcc/fcc solid three phases equilibria in the Fe–Ni–Cr system between 1770 and 1625 K. Fig. 7 illustrates the temperature development of only existing bcc/fcc solid equilibria by four isothermal sections between 1573 and 1273 K. Finally Fig. 8 shows the isothermal sections at 1173 and 1073 K involving the σ-phase.

At 1873 K the isothermal section shows in Fig. 5a the liquid/bcc solid equilibria existing only. Three-phase region starts at the peritectic temperature in the Fe–Ni system at 1786 K (compare Fig. 3a). Also plotted in Fig. 5a is the isothermal section of the Fe–Ni–Cr system at 1770 K. We can notice from Fig. 5a that the liquid/fcc solid equilibria lines as computed in this work agree reasonably with the experimental results of Schüttmann et al. [26], and Kundrat and Elliott [3]. As reported already in [16], the liquidus lines of the assessments of the latter authors, and of Hillert and Qiu [8] show distinctly less agreement with experimental points than the optimization based upon mass spectrometric data of the ternary Fe–Ni–Cr alloys. In Fig. 5b the phase equilibrium lines as computed in this work at 1723 K are compared with the results of the calculations by Hasebe and Nishizawa [6]. The severe discrepancies

Fig. 5. Isothermal sections of Fe–Ni–Cr system involving liquid phase. (a) This work at 1873 K (—) and at 1770 K (—); experimental points of fcc–liquid equilibria at 1770 K: Schüttmann et al. [26] (○); Kundrat and Elliott [3] (○). (b) This work at 1723 K (—); Hasebe and Nishizawa [6] (—). (c) This work at 1673 K (—) and at 1625 K (—).
between the course of fcc/liquid equilibrium lines may be caused by the evaluated zero value of ternary interaction parameters in [6]. Finally Fig. 5c shows the results of the phase equilibria synthesis of this investigations at 1675 and 1625 K.

The resultant temperature development of the liquid/bcc/fcc three phases equilibria as presented in Fig. 6 in steps of 20-25 K (gray fields) yields liquidus and fcc solidus lines between 1775 K (binary Fe-Ni) and 1618 K (binary Ni-Cr) showing even a better agreement with the experimentally determined points than the results of the previous assessments (see also [16]). Fig. 1 illustrates, that the temperature dependence of the distribution coefficients of Ni and Cr as obtained in this work clearly shows better agreement with experimental data than the computed curves from Hiltbert and Qiu [8] and Lee [9]. However, the melting and solidification temperatures of the binary Fe-Ni alloys cover only a small temperature interval of about 100 K over the whole range of compositions, and the two binary boundary systems Fe-Ni and Cr-Fe show very narrow liquid-solid two-phase regions, as obviously from Fig. 3. We cannot therefore expect too precise determinations of the temperature dependencies of the corresponding binary and ternary equilibrium compositions.

The optimization of this work yielded fcc–bcc phase equilibria which are in excellent agreement with the experimental phase diagram information. Fig. 7a illustrates this for the isothermal sections at 1573 and 1473 K, comparing the computed tie lines of this work with the experimental points reported by Mundt and Hoffmeister [31] for these temperatures, and by Hasebe and Nishizawa [6] and Schultz and Merrick [32] for 1473 K. In Fig. 7b the results of this assessment at 1373 and 1273 K are plotted together with the experimental points determined by Hasebe and Nishizawa [6] at these temperatures, as well as by Schultz and Merrick [32] and Chiba [33] at 1373 K.

The isothermal sections involving the ω-phase at 1173 and 1073 K show also satisfactory agreement of the results of this assessment with the corresponding experimental information (Fig. 8). At 1173 K full agreement is achieved with the measurements as reported by Sopousek and Krunl [4] and Hasebe and Nishizawa [6] and Schirmann et al. [26] (Fig. 8a). As can be seen from Fig. 8b, at 1073 K also satisfactory agreement is obtained with the experimental points from Sopousek and Krunl [4] and Rees et al. [34]. The agreement between experimental and calculated equilibrium composition values is again better than in calculations using
6. Conclusion

In this work the computational synthesis of the phase equilibria curves of ternary Fe–Ni–Cr alloys has been based upon substantial more experimental data of the thermodynamic mixing behavior than previous attempts. This yields a distinct improved overall-agreement with the experimental phase literature than the results of previous assessments. The thermodynamic description used in this work is simpler than that of previous assessments, and restricted the magnetic correction to the terms of pure components only. This raises the suspicion that especially at temperatures above the Néel or Curie temperatures the use of binary magnetic corrections will only improve the quality of binary phase diagrams in cases of employing a bit doubtful excess data.

Complete thermodynamic parameter sets of all three binary boundary systems as well as the new ternary interaction terms are presented. Several isothermal and vertical sections as well as various projections of the Fe–Ni–Cr phase diagram in the temperature range from 1073 to 1873 K illustrate reliability of the new description. The thermodynamic parameters of this investigation yield better reproducing of the distribution coefficients of Cr and Ni than data assessed previously.

Oates et al. [35] required to put more physics into CALPHAD solution models. And even Hillert, the founder and mentor of the ThermoCalc group, regretted some developments in the phase diagram engineering at the CALPHAD XXVI Conference. He was concerned that CALPHAD had reached a stage where its future scientific status might be in danger [36]. Omitting the problematic splitting of the excess contribution in favor of employing thermodynamic mixing properties more experimentally proved, may be the right way doing this.

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References


