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DETERMINATION OF INTERCHANGE ENERGIES FROM THERMODYNAMIC AND STRUCTURAL DATA

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Introduction. — The statistical model calculations describing the ordering and segregation reactions in solid solutions are generally formulated in terms of temperature and composition independent energy parameters $W(k)$ between $k$th neighbours which are defined by the relation

$$W(k) = -2V^k_{AB} + V^k_{AA} + V^k_{BB}$$

where $V^k_{ij}$ are pairwise interaction energies [1-2]. For an ordering tendency in the $k$th neighbourhood $W(k)$ is positive, negative values correspond to a segregation tendency. It is generally presumed that $W(k)$ decreases with increasing $k$.

In bcc solid solutions ordering reactions between nearest (1 nn) and second nearest neighbours (2 nn) are observed experimentally (Fe-Al [3-4], Fe-Si [5-6]). Therefore in bcc alloys at least two parameters $W^{(1)}$ and $W^{(2)}$ are required for a description of the observed ordering reactions. In fcc solid solutions only ordering reactions between 1 nn are found experimentally (Fe-Pt, Fe-Ni, Co-Pt, NiPt [7]). Therefore it is generally presumed that the ordering reactions in fcc alloys should be describable with a single energy parameter $W^{(1)}$. It will be shown, however, that the coupling of structural and thermodynamic data implies the presence of strong contributions from 2 nn in fcc alloys, too.

**Determination of $W(k)$ from Energy Measurements.** — Since $W(k)$ are energy parameters, they are most easily determined from energy measurements like enthalpies of mixing of random alloys or enthalpies of formation $\delta H(c, T)$ of alloys with given atomic configurations. These entities can immediately be expressed by means of $W(k)$ for a binary alloy $A_1-cB_2$ with reference to the pure components in the same crystal structure as the alloy formed, e.g. bcc [8] :

$$\delta H^{A2}_{(G)} = -Nc(1-c)(4W^{(1)} + 3W^{(2)})$$

$$\delta H^{A2}_{(G,T = OK)} = -N[c(4W^{(1)} + 3W^{(2)}) - 6c^2 W^{(2)}] \quad \text{for} \quad 0 \leq c \leq 0.5$$

$$\delta H^{B2}_{(G,T = OK)} = -N[1.5W^{(2)} + c(4W^{(1)} - 3W^{(2)})] \quad \text{for} \quad 0.25 \leq c \leq 0.5$$

$$\delta H^{B2}_{(G,T = OK)} = -N[c(4W^{(1)} + 3W^{(2)}) - 4c^2 W^{(1)}] \quad \text{for} \quad c \leq 0.5.$$
Similarly one gets for fcc solid solutions

\[ F_{Hc}^{(1)} = -Nc(1 - c)(6W^{(1)} + 3W^{(2)}) \]  
\[ F_{Hc}^{(1)} = -N[6W^{(1)} + 3W^{(2)}] \text{ for } c \leq 0.5 \]  
\[ F_{Hc}^{(1)} = -N[6W^{(1)} + 3W^{(2)} - c^2(4W^{(1)} + 6W^{(2)})] \text{ for } 0 \leq c \leq 0.25 \]  
\[ F_{Hc}^{(1)} = -N[6W^{(1)} - 1.5W^{(2)} + c(2W^{(1)} + 9W^{(2)}) - 12c^2W^{(2)}] \text{ for } 0.25 \leq c \leq 0.5 \]  

Here \( N \) is the total number of atoms. The label \( T = OK \) indicates that the expressions (2)-(5) and (7)-(9) hold for the completely long range ordered alloys.

If the experimental enthalpies of formation refer to standard states of the pure components with crystal structures differing from the one of the alloy formed, these data must be converted as described in [8]. An additional conversion is necessary if ferromagnetic alloys or components are considered. These conversions have been discussed [8] and applied [9-10] elsewhere.

**DETERMINATION OF \( W^{(k)} \) FROM CRITICAL TEMPERATURES.** — The critical temperatures of long range order (lro) can be connected with the interchange energies \( W^{(k)} \) only by means of statistical models. Due to the different approximations in the various models the interchange energies \( W^{(k)} \) as determined from energy measurements yield different critical temperatures \( T_{\text{crit}}^{\text{model}} \). The simplest approximation (Bragg-Williams-Gorsky (BWG)) yields analytical expressions for the uppermost critical temperatures \( T_{\text{crit}}^{\text{BWG}} \) in terms of \( c \) and \( W^{(k)} \) [8]. Its advantage is the minor numerical work as compared to the actually most sophisticated cluster variation (CV) method [11-12]. It has been shown for bcc alloys [8] that as far as a determination of \( W^{(k)} \) from critical temperatures is concerned the CV-results can be used if \( T_{\text{crit}}^{\text{CV}} \) is corrected by a temperature scale factor \( \kappa \) which numerical value depends on the ratio \( W^{(2)}/W^{(1)} \):

\[ T_{\text{crit}}^{\text{real}} = \kappa T_{\text{crit}}^{\text{BWG}} \]

The numerical values of \( \kappa \), see figure 1, have been estimated taking for the real critical temperature at \( c = 0.5 \) the CV-result \( T_{\text{crit}}^{\text{CV}} \). Thereby it turned out that fortunately the experimental critical temperatures follow the temperature scaled BWG-results \( T_{\text{crit}} = \kappa T_{\text{crit}}^{\text{BWG}} \) more closely than the original CV-results. For fcc alloys the CV-calculations have only been done with \( W^{(2)} = 0 \) [11-12]. The results are shown in figure 2 together with the BWG-results for \( W^{(1)} = 1000 K, W^{(2)} = 0 \). Therefrom one gets \( \kappa = 0.5 \). With this value the corrected BWG- and the CV-results are shown in figure 3. There remain differences which are not of importance as far as the \( W^{(k)} \)-determination is concerned.

**Fig. 1.** — Temperature scale factor \( \kappa \) for bcc solid solutions which formally corrects the BWG-results for sro effects [8], in dependence on the ratio of second nearest to nearest neighbour interchange energies.

**Fig. 2.** — Phase diagrams for a given set of numerical values of the interchange energies, calculated according to the BWG- and CV-models. Hatched lines indicate continuous transitions.

**Fig. 3.** — Comparison of the temperature scaled BWG phase diagram (full lines) (\( \kappa = 0.5 \)) with the CV diagram (broken lines) (\( W^{(1)} > 0, W^{(2)} = 0 \)). Hatched lines indicate continuous transitions.
It is thus proposed to determine the $W^{(k)}$ using the sro-corrected BWG-formulae for the uppermost critical temperature:

\begin{align*}
bcc: & \quad k T_{(0)}^{2 \rightarrow A2} = \kappa \cdot c (1 - c) (8 W^{(1)} - 6 W^{(2)}) \quad (10) \\
& \quad k T_{(0)}^{O0 \rightarrow A2} = \kappa \cdot c (1 - c) 6 W^{(2)} \quad (11) \\
& \quad k T_{(c)}^{B2 \rightarrow A2} = \kappa \cdot c (1 - c) 6 W^{(3)} \quad (12)
\end{align*}

It depends on the ratio $W^{(2)}/W^{(1)}$ which transition exhibits the highest critical temperature for a given composition, see [13].

For bcc alloys, the value of $\kappa$ must be taken from figure 1. It is to be expected that in fcc alloys the value of $\kappa$ also varies in the range $0.5 \leq \kappa \leq 0.9$ with $W^{(2)}/W^{(1)}$. However, in view of the lack of CV-calculations for fcc alloys with $W^{(2)} \neq 0$ the value $\kappa = 0.5$ will be used throughout. Other values of $\kappa$ within the expected range do not alter qualitatively the conclusions drawn for the fcc alloys considered here.

**Results for bcc alloys.** — The application of the proposed method of determination of the values for $W^{(1)}$, $W^{(2)}$ has already been described in [9-10]. The resulting values of this treatment are summarized in table I. It could be shown that with these values reliable values of other physical entities, e.g. anti-phase boundary energies of ordered alloys, the enthalpy of transformation $\Delta H^{bcc\rightarrow diamond}$, could be calculated.

**TABLE I**

Chemical interchange energies $W^{(1)}$, $W^{(2)}$ and correction factor $\kappa$ for sro effects of bcc and fcc binary alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$W^{(1)}$[k]</th>
<th>$W^{(2)}$[k]</th>
<th>$\kappa$</th>
<th>Structure</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Au</td>
<td>455</td>
<td>535</td>
<td>0.70</td>
<td>bcc (*)</td>
<td>[9]</td>
</tr>
<tr>
<td>Ag-Zn</td>
<td>585</td>
<td>300</td>
<td>0.70</td>
<td>bcc</td>
<td>[9]</td>
</tr>
<tr>
<td>Au-Cu</td>
<td>1 210</td>
<td>660</td>
<td>0.68</td>
<td>bcc (*)</td>
<td>[9]</td>
</tr>
<tr>
<td>Au-Zn</td>
<td>1 785</td>
<td>1 000</td>
<td>0.67</td>
<td>bcc</td>
<td>[9]</td>
</tr>
<tr>
<td>Cu-Zn</td>
<td>955</td>
<td>535</td>
<td>0.67</td>
<td>bcc</td>
<td>[9]</td>
</tr>
<tr>
<td>Fe-Ti</td>
<td>1 570</td>
<td>1 125</td>
<td>0.80</td>
<td>bcc</td>
<td>[9]</td>
</tr>
<tr>
<td>Fe-Co</td>
<td>500</td>
<td>0</td>
<td>0.8</td>
<td>bcc</td>
<td>[10]</td>
</tr>
<tr>
<td>Fe-Si</td>
<td>2 830</td>
<td>1 410</td>
<td>0.71</td>
<td>bcc</td>
<td>[10]</td>
</tr>
<tr>
<td>Fe-Pt</td>
<td>1 250</td>
<td>1 250</td>
<td>0.5 (*)</td>
<td>fcc</td>
<td></td>
</tr>
<tr>
<td>Co-Pt</td>
<td>1 140</td>
<td>710</td>
<td>0.5 (*)</td>
<td>fcc</td>
<td></td>
</tr>
<tr>
<td>Ni-Pt</td>
<td>1 000</td>
<td>533</td>
<td>0.5 (*)</td>
<td>fcc</td>
<td></td>
</tr>
<tr>
<td>Cu-Au</td>
<td>755</td>
<td>407</td>
<td>0.5 (*)</td>
<td>fcc</td>
<td></td>
</tr>
<tr>
<td>Fe-Ni</td>
<td>675</td>
<td>683</td>
<td>0.5 (*)</td>
<td>fcc</td>
<td>[20]</td>
</tr>
</tbody>
</table>

(* Values for hypothetical bcc alloys derived from ternary bcc alloy data.

The value $\kappa = 0.5$ is provisional (see text). Therefore the same must be reminded for $W^{(1)}$, $W^{(2)}$ derived with this value.

**Results for fcc alloys.** — The essential result obtained with the present treatment is that $W^{(2)}$ is by far not zero. This is best visualized by the following argument: if $W^{(2)}$ were zero or at least negligible it would follow from eqs. (6) and (13) that the critical temperature $T_{L}^{10-A1}(0.5)$, at $c = 0.5$, which at this composition is identical with $T_{L}^{10-A1}$, should be linearly related with the enthalpy of formation of the random alloy at $c = 0.5$:

$$F H_{(0.5)}^{(A1)} = \frac{3}{2} k N T_{L}^{10-A1}(0.5) = - 3 k N T_{L}^{10-A1}.$$  

(14)

In figure 4 this linear relation is shown as a straight line. Also indicated are the available experimental values which do not follow the relation (14). This discrepancy can be removed if one takes account of 2 nn-interactions. Then two experimental informations are needed to determine $W^{(1)}$ and $W^{(2)}$.

$$Fe-Pt. \quad T^{10-A1} = 1 553 K \quad [14] \quad \text{and} \quad F H_{(0.5)}^{(10-A1)} = - 20.9 \text{kJ/mole}$$

of Fe$_{0.5}$Pt$_{0.5}$ [15]. Since $T = 1 123 K$ is sufficiently below $T^{10-A1}$ to set the enthalpy of formation at

\[ \text{FIG. 4.} - \text{Enthalpies of mixing of random fcc alloys with reference to fcc pure components versus maximum critical temperature of } \text{Iro at } c = 0.5. \text{ The solid line represents the relationship which should be obeyed if } W^{(2)} = 0; \text{ the experimental values; } \star \text{ the experimental values (O) contain sro and/or magnetic contributions (see text) which are shown by the arrows.} \]
1 123 K equal to $F(0.5, T = 0 \text{ K})$ \cite{12, 16} one gets from eqs. (7) and (13) the interchange energies in table I.

$$Co_{0.5}Pt \quad T_{(0.5)}^{L10-A1} \simeq 1 100 \text{ K} \ [7, 17]$$

$$F(0.5, 1 133 \text{ K}) = -10.8 \text{ kJ/mole}$$

of $Co_{0.5}Pt_{0.5}$ \cite{18}. At 1 133 K pure Co is ferromagnetic (fm) whereas the alloy formed is paramagnetic (pm). By means of the procedures outlined in \cite{8, 10} one gets for the enthalpy of transformation

$$\Delta^0H_{Cu(110 \text{ K})}^{\text{fem-pm}} \approx 7 300 \text{ J/mol}$$

In addition it has to be considered that at $T = 1 133 \text{ K}$, i.e. just above the critical temperature, the enthalpy of formation contains a sro contribution which, according to the CV-model, should amount to half the total enthalpy $\Delta H_{L10-A1}^{(0.5)}$ \cite{12, 16}. It follows from eqs. (6), (7), (13):

$$\Delta H_{L10-A1}^{(0.5)} = \frac{kN}{2 K} T_{(0.5)}^{L10-A1}$$

Thus one gets:

$$F_{(0.5)}^{A1} = -10.8 - \frac{1}{2} \Delta^0H_{Cu}^{\text{fem-pm}} (1 133 \text{ K}) + \frac{1}{2} \frac{kN}{2 K} T_{(0.5)}^{L10-A1}$$

Inserting the numerical data and using eqs. (6) and (13) one gets the values for $W^{(1)}$, $W^{(2)}$ in table I.

$$Ni_{0.5}Pt \quad T_{(0.5)}^{L10-A1} \simeq 900 \text{ K} \ [7, 17]$$

$$F_{(0.5)}^{A1} = -9.2 \text{ kJ/mole}$$

of $Ni_{0.5}Pt_{0.5}$ \cite{19}. Therefrom the values in table I have been deduced as above.

$Fe_{0.5}Ni$. — In this instance chemical and magnetic interactions must be considered. The final result of this treatment \cite{20} is also included in table I.

$$Cu_{0.5}Au_{0.5} \quad T_{(0.5)}^{L10-A1} \simeq 683 \text{ K} \ [7]$$

$$F_{(0.5,800K)}^{A1} = -9.2 \text{ kJ/mole}$$

of $Cu_{0.5}Au_{0.5}$ \cite{21}. According to the CV-model, at $T = 800 \text{ K}$, there should be contained about 40 % of $\Delta H_{(0.5,0}^{A1})$ as sro-contribution in the experimental value. The same treatment of getting $F_{(0.5)}^{A1}$ as applied to Co-Pt yields the values of $W^{(1)}$, $W^{(2)}$ in table I.

Conclusions. — For the fcc alloys considered here it can be concluded that the coupling of energetic and structural data leads to negative interchange energies between 2 nn. The consequences for the phase diagram are shown in figures 5a and 5b where the phase diagrams calculated in the BWG-approximation with two sets of negative values for $W^{(2)}$ are represented: at $T = 0 \text{ K}$ heterogeneous ground states are predicted (see also \cite{22}) which extend to higher temperatures the more negative $W^{(2)}$ becomes.

![Phase diagram](image)

**Fig. 5.** — Phase diagrams according to the BWG-model for $W^{(1)} > 0$ and $W^{(2)} = -0.5 W$ (Fig. 5a) or $W^{(2)} = -2 W^{(1)}$ (Fig. 5b).

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References


