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► To cite this version:

G. Inden. DETERMINATION OF INTERCHANGE ENERGIES FROM THERMODYNAMIC AND STRUCTURAL DATA. Journal de Physique Colloques, 1977, 38 (C7), pp.C7-373-C7-377. 10.1051/jphyscol:1977774 . jpa-00217277

HAL Id: jpa-00217277

<https://hal.science/jpa-00217277>

Submitted on 1 Jan 1977

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DETERMINATION OF INTERCHANGE ENERGIES FROM THERMODYNAMIC AND STRUCTURAL DATA

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Résumé. — Les valeurs numériques des énergies d'échange $W^{(1)}$, $W^{(2)}$ entre premiers et seconds voisins dans des solutions solides cfc et cc peuvent être déterminées à partir de données énergétiques (p.e. enthalpies de formation) et de données structurales (p.e. températures critiques). Si les données énergétiques ne réfèrent pas à des états standards cfc (ou cc), elles doivent être transformées par une conversion appropriée. Si l'on utilise des températures critiques il faut tenir compte d'effets d'ordre à courte distance. Dans le cas des solutions cfc et cc étudiées l'on trouve des valeurs de $W^{(1)}$, $W^{(2)}$ de même ordre de magnitude. En cas d'alliages cfc cependant $W^{(2)}$ est de signe opposé de $W^{(1)}$. Les conséquences qui en résultent pour les diagrammes de phase sont présentées.

Abstract. — The numerical values of the interchange energies $W^{(1)}$, $W^{(2)}$ between nearest and next-nearest neighbours in bcc and fcc solid solutions can be determined from energy measurements (e.g. enthalpy of formation) and from structural data (e.g. critical temperature of long range order). If the energy data do not refer to bcc (or fcc) standard states they must be appropriately converted. If critical temperatures are used short range order effects must be considered. For both fcc and bcc solid solutions $W^{(1)}$ and $W^{(2)}$ are found of the same order of magnitude. In the fcc alloys studied here $W^{(2)}$ is found of opposite sign of $W^{(1)}$. The consequences for the phase diagram are discussed.

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

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

where $V_{ij}^{(k)}$ 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 $^F H(c, T)$ of alloys with given atomic configurations. These entities can immediately be expressed by means of $W^{(k)}$ for a binary alloy $A_{1-c}B_c$ with reference to the pure components in the same crystal structure as the alloy formed, e.g. bcc [8] :

$$^F H_{(c)}^{A_2} = -Nc(1-c)(4W^{(1)} + 3W^{(2)}) \quad (1)$$

$$^F H_{(c,T=OK)}^{B_2} = -N[c(4W^{(1)} + 3W^{(2)}) - 6c^2W^{(2)}] \text{ for } c \leq 0.5 \quad (2)$$

$$^F H_{(c,T=OK)}^{DO_3} = -Nc(4W^{(1)} + 3W^{(2)}) \text{ for } 0 \leq c \leq 0.25 \quad (3)$$

$$= -N[1.5W^{(2)} + c(4W^{(1)} - 3W^{(2)})] \text{ for } 0.25 \leq c \leq 0.5 \quad (4)$$

$$^F H_{(c,T=OK)}^{B_3^2} = -N[c(4W^{(1)} + 3W^{(2)}) - 4c^2W^{(1)}] \text{ for } c \leq 0.5. \quad (5)$$

Similarly one gets for fcc solid solutions

$${}^F H_{(c)}^{A1} = -Nc(1-c)(6W^{(1)} + 3W^{(2)}) \quad (6)$$

$${}^F H_{(c,T=OK)}^{L10} = -N[c(6W^{(1)} + 3W^{(2)}) - c^2(4W^{(1)} + 6W^{(2)})] \text{ for } c \leq 0.5 \quad (7)$$

$${}^F H_{(c,T=OK)}^{L12} = -N[c(6W^{(1)} + 3W^{(2)}) - 12c^2W^{(2)}] \text{ for } 0 \leq c \leq 0.25 \quad (8)$$

$${}^F H_{(c,T=OK)}^{Pmmm} = -N[W^{(1)} - 1.5W^{(2)} + c(2W^{(1)} + 9W^{(2)}) - 12c^2W^{(2)}] \text{ for } 0.25 \leq c \leq 0.5. \quad (9)$$

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_{crit}^{model} . The simplest approximation (Bragg-Williams-Gorsky (BWG)) yields analytical expressions for the uppermost critical temperatures T_{crit}^{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 BWG-results can be used if T_{crit}^{BWG} is corrected by a temperature scale factor κ which

FIG. 1. — Temperature scale factor κ 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.

numerical value depends on the ratio $W^{(2)}/W^{(1)}$: $T_{crit}^{real} = \kappa T_{crit}^{BWG}$. The numerical values of κ , see figure 1, have been estimated taking for the real critical temperature at $c = 0.5$ the CV-result $T_{crit(0.5)}^{CV}$. Thereby it turned out that fortunately the experimental critical temperatures follow the temperature scaled BWG-results $T_{crit} = \kappa T_{crit}^{BWG}$ 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. 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 :

$$\text{bcc} : kT_{(c)}^{B2 \rightarrow A2} = \kappa \cdot c(1 - c) (8 W^{(1)} - 6 W^{(2)}) \quad (10)$$

$$kT_{(c)}^{DO_3 \rightarrow A2} = \kappa \cdot c(1 - c) 6 W^{(2)} \quad (11)$$

$$kT_{(c)}^{B32 \rightarrow A2} = \kappa \cdot c(1 - c) 6 W^{(2)} \quad (12)$$

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

$$\text{fcc} : kT_{(c)}^{L12 \rightarrow A1} = \kappa \cdot c(1 - c) (4 W^{(1)} - 6 W^{(2)}) \quad (13)$$

For bcc alloys, the value of κ must be taken from figure 1. It is to be expected that in fcc alloys the value of κ 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 κ 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 $\Delta H_{Si}^{bcc \rightarrow \text{diamond}}$, could be calculated.

TABLE I

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

$$([k] = 1 \text{ k-unit} = 13.8 \times 10^{-24} \text{ J} = 8.6 \times 10^{-5} \text{ eV})$$

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

^(a) Values for hypothetical bcc alloys derived from ternary bcc alloy data.

^(b) 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 $T_{(0.5)}^{L12 \rightarrow A1}$, at $c = 0.5$, which at this composition is identical with $T_{(0.5)}^{L10 \rightarrow A1}$, should be linearly related with the enthalpy of formation of the random alloy at $c = 0.5$:

$$^F H_{(0.5)}^{A1} = -\frac{3}{2\kappa} kNT_{(0.5)}^{L10 \rightarrow A1} = -3 kNT_{(0.5)}^{L10 \rightarrow A1} \quad (14)$$

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

FIG. 4. — Enthalpies of mixing of random fcc alloys with reference to fcc pure components versus maximum critical temperature of Fe at $c = 0.5$. The solid line represents the relationship which should be obeyed if $W^{(2)} = 0$; ● experimental values; ★ the experimental values (O) contain sro and/or magnetic contributions (see text) which are shown by the arrows.

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. — $T_{(0.5)}^{L10 \rightarrow A1} = 1 553 \text{ K}$ [14] and

$$^F H(0.5, 1 123 \text{ K}) = -20.9 \text{ kJ/mole}$$

of $\text{Fe}_{0.5}\text{Pt}_{0.5}$ [15]. Since $T = 1 123 \text{ K}$ is sufficiently below $T_{(0.5)}^{L10 \rightarrow A1}$ to set the enthalpy of formation at

1 123 K equal to ${}^F H(0.5, T = 0 \text{ K})$ [12, 16] one gets from eqs. (7) and (13) the interchange energies in table I.

Co-Pt. — $T_{(0.5)}^{L_{10} \rightarrow A1} \simeq 1\,100 \text{ K}$ [7, 17] and

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

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

$$\Delta^0 H_{\text{Co}(1133 \text{ K})}^{\text{fm} \rightarrow \text{pm}} \simeq 7\,300 \text{ J/mol}.$$

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 $\Delta H_{(0.5)}^{L_{10} \rightarrow A1}$ [12, 16]. It follows from eqs. (6), (7), (13) :

$$\Delta H_{(0.5)}^{L_{10} \rightarrow A1} = \frac{kN}{2\kappa} T_{(0.5)}^{L_{10} \rightarrow A1}.$$

Thus one gets :

$${}^F H_{(0.5)}^{A1} = -10.8 - \frac{1}{2} \Delta^0 H_{\text{Co}}^{\text{fm} \rightarrow \text{pm}}(1\,133 \text{ K}) + \frac{1}{2} \frac{kN}{2\kappa} T_{(0.5)}^{L_{10} \rightarrow A1}.$$

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

Ni-Pt. — $T_{(0.5)}^{L_{10} \rightarrow A1} \simeq 900 \text{ K}$ [7, 17] and

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

of $\text{Ni}_{0.5}\text{Pt}_{0.5}$ [19]. Therefrom the values in table I have been deduced as above.

Fe-Ni. — In this instance chemical and magnetic interactions must be considered. The final result of this treatment [20] is also included in table I.

Cu-Au. — $T_{(0.5)}^{L_{10} \rightarrow A1} = 683 \text{ K}$ [7] and

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

of $\text{Cu}_{0.5}\text{Au}_{0.5}$ [21]. According to the CV-model, at $T = 800 \text{ K}$, there should be contained about 40 % of $\Delta H_{(0.5, 0 \text{ K})}^{L_{10} \rightarrow A1}$ as sro-contribution in the experimental value. The same treatment of getting ${}^F H_{(0.5)}^{A1}$ 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 [22]) which extend to higher temperatures the more negative $W^{(2)}$ becomes.

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

Acknowledgment. — The author wishes to thank Prof. W. Pitsch, Düsseldorf, for many discussions. The financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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