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The Influence of Second-Nearest Neighbor Interactions on the Thermodynamic Properties of B2 Phases with Substitutional Defects

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With 5 Figures

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In order to explain some discrepancies between the theoretical predictions and the experimental data for the thermodynamic properties of substitutional B 2 phases, *Chang's* theoretical model is extended by including the influence of second-nearest neighbor interactions. For this purpose a new parameter η is introduced which is defined as the ratio of the interchange energies between second-nearest and first-nearest neighbors. Theoretical equations are derived for the compositional dependence of the activity and the partial molar enthalpy. Using literature data, the following phases are re-evaluated in terms of the disorder parameter α and the newly introduced parameter η: β'-AuZn, β'-AuCd, β'-AgMg, and β'-NiZn. Very good agreement is found between the theoretical curves and the experimental data for the four systems. The values of η obtained range from 0.0 for β'-NiZn to 0.5 for β'-AuZn. The inclusion of second-nearest neighbor interactions has little influence on the values of α. It is shown that the behavior of the activity curve in β'-AuZn can be explained in a physically more meaningful way by including interactions between all second-nearest neighbors rather than interactions between gold substitutional defects only, as was done by *Libowitz.*

1. Introduction

In a series of publications, *Chang* and co-workers[1–6] have developed theoretical expressions for the thermodynamic properties of ordered intermetallic phases exhibiting the B 2, $L1_0$, and $L1_2$ structures.

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[*] Auf Karenz-Urlaub vom Institut für Anorganische Chemie der Universität Wien, Österreich.

These theoretical equations were compared with experimental data for a large number of intermetallic phases[1–11]; satisfactory agreement was obtained for most of the alloy phases with the notable exception of β′-AuZn, which exhibits the B 2 structure with substitutional defects. In this case, significant discrepancies between the theoretical activity curve and the experimental data were observed for even moderate deviations from stoichiometry. In the development of their theoretical model for B 2 phases, *Chang* and co-workers considered only first nearest neighbor interactions, and it appears quite possible that the discrepancies in the case of β′-AuZn may be due to the neglect of the interactions between second-nearest neighbors. The objective of the present study is to derive theoretical equations for the thermodynamic properties of substitutional B 2 phases considering both first-nearest and second-nearest neighbor interactions, and to test their validity with available experimental data.

2. Theoretical Development

2.1. *Integral Enthalpy*

A crystal lattice of the B 2-type can be divided into two simple cubic sublattices which may be called the α- and the β-sublattice; in the perfect crystal, the **A** atoms occupy the α-sites and the **B** atoms the β-sites. Considering substitutional defects, the contributions of first-nearest and second-nearest neighbor interactions yield the following expression for the integral enthalpy:

$$\begin{aligned} H = {} & [n_{\mathbf{A}(\alpha)\mathbf{B}(\beta)} + n_{\mathbf{A}(\beta)\mathbf{B}(\alpha)}]\, H_{\mathbf{AB}} + n_{\mathbf{A}(\alpha)\mathbf{A}(\beta)} H_{\mathbf{AA}} + n_{\mathbf{B}(\alpha)\mathbf{B}(\beta)}\, H_{\mathbf{BB}} + \\ & + [n_{\mathbf{A}(\alpha)\mathbf{B}(\alpha)} + n_{\mathbf{A}(\beta)\mathbf{B}(\beta)}]\, H'_{\mathbf{AB}} + [n_{\mathbf{A}(\alpha)\mathbf{A}(\alpha)} + n_{\mathbf{A}(\beta)\mathbf{A}(\beta)}]\, H'_{\mathbf{AA}} + \\ & + [n_{\mathbf{B}(\alpha)\mathbf{B}(\alpha)} + n_{\mathbf{B}(\beta)\mathbf{B}(\beta)}]\, H'_{\mathbf{BB}}. \end{aligned} \tag{1}$$

In Eq. (1), H_{ij} is the interaction enthalpy for a pair of atoms i–j at a distance of $0.866a$ (first-nearest neighbors) and H'_{ij} that for a pair i–j at a distance of a (second-nearest neighbors) where a is the lattice parameter; $n_{i(\alpha)\,j(\beta)}$ is the number of pairs of atoms i–j; the Greek letters in parentheses indicate the sublattice, on which the corresponding atoms are located. As in the previous work[1–5] the degree of disorder z, at any composition χ, is defined as:

$$z \equiv \left(\frac{N^{\beta}_{\mathbf{A}}}{N}\right)_{\chi}, \tag{2}$$

where $N^{\beta}_{\mathbf{A}}$ is the number of **A** atoms on the β-sublattice, N is the total number of atoms, and $\chi = x_{\mathbf{B}} - 0.5$, with $x_{\mathbf{B}}$ being the atom fraction of **B** in the alloy. The value of z for $\chi = 0$, i.e. at the stoichiometric composition, is defined as the disorder parameter α:

$$\alpha \equiv \left(\frac{N^{\beta}_{\mathbf{A}}}{N}\right)_{\chi = 0} \equiv \left(\frac{N^{\alpha}_{\mathbf{B}}}{N}\right)_{\chi = 0}, \tag{3}$$

where $N^{\alpha}_{\mathbf{B}}$ is the number of **B** atoms on the α-sublattice.

Table 1. *Atomic Distributions on the* α- *and* β-*Sublattices for B 2 Phases with Substitutional Defects*

No. of Sites		Total Atoms N	α-Sublattice $N/2$	β-Sublattice $N/2$
$\chi \neq 0$	**A** atoms	$N_{\mathbf{A}} = (1/2 - \chi)N$	$N^{\alpha}_{\mathbf{A}} = (1/2 - \chi - z)N$	$N^{\beta}_{\mathbf{A}} = zN$
	B atoms	$N_{\mathbf{B}} = (1/2 + \chi)N$	$N^{\alpha}_{\mathbf{B}} = (\chi + z)N$	$N^{\beta}_{\mathbf{B}} = (1/2 - z)N$
$\chi = 0$	**A** atoms	$N_{\mathbf{A}} = N/2$	$N^{\alpha}_{\mathbf{A}} = (1/2 - \alpha)N$	$N^{\beta}_{\mathbf{A}} = \alpha N$
	B atoms	$N_{\mathbf{B}} = N/2$	$N^{\alpha}_{\mathbf{B}} = \alpha N$	$N^{\beta}_{\mathbf{B}} = (1/2 - \alpha)N$

Expressing the numbers of the different interactions in terms of χ and z on the basis of the atomic distribution on the two sublattices (see Table 1) and the coordination numbers for first- and second-nearest neighbors, which are eight and six, resp., Eq. (1) becomes:

$$\begin{aligned} H = \frac{N}{2} \{ & 8\,[(2z^2 + 2\chi z - z)\,4\,V_{\mathbf{AB}} - (2z^2 + 2\chi z - z + \chi^2)\,3\,V'_{\mathbf{AB}}] + \\ & + 4\,(2 - 4\chi)\,H_{\mathbf{AB}} + 12\chi H'_{\mathbf{AB}} + 3\,(1 - 4\chi)\,H'_{\mathbf{AA}} + \\ & + 16\chi H_{\mathbf{BB}} + 3H'_{\mathbf{BB}}\}. \end{aligned} \tag{4}$$

$V_{\mathbf{AB}}$ and $V'_{\mathbf{AB}}$ are the interchange energies between first- and second-nearest neighbors, resp.:

$$V_{\mathbf{AB}} = H_{\mathbf{AB}} - \frac{1}{2}\,(H_{\mathbf{AA}} + H_{\mathbf{BB}}), \tag{5a}$$

$$V'_{\mathbf{AB}} = H'_{\mathbf{AB}} - \frac{1}{2}\,(H'_{\mathbf{AA}} + H'_{\mathbf{BB}}). \tag{5b}$$

By introducing a new parameter η, defined as:

$$\eta = \frac{V'_{\mathbf{AB}}}{V_{\mathbf{AB}}} \tag{6}$$

Eq. (4) can be written as

$$\begin{aligned} H = \frac{N}{2} \{ & 8[(2z^2 + 2\chi z - z)(4 - 3\eta) V_{\mathbf{AB}} - 3\eta \chi^2 V_{\mathbf{AB}}] + \\ & + 4(2 - 4\chi) H_{\mathbf{AB}} + 12\chi H'_{\mathbf{AB}} + 3(1 - 4\chi) H'_{\mathbf{AA}} + \\ & + 16\chi H_{\mathbf{BB}} + 3H'_{\mathbf{BB}} \}. \end{aligned} \tag{7}$$

2.2. *Integral Entropy*

Since the consideration of interactions between second-nearest neighbors does not change the expression for the integral configurational entropy S_c, Eq. (21) in Ref. [5] derived for B 2 phases with substitutional defects can be taken directly:

$$\begin{aligned} S_c = -\frac{1}{2} R \, [& 2z \ln(2z) + (1 - 2z) \ln(1 - 2z) + 2(\chi + z) \ln 2(\chi + z) + \\ & + (1 - 2\chi - 2z) \ln(1 - 2\chi - 2z)]. \end{aligned} \tag{8}$$

As before, all other contributions to the entropy are assumed to be composition independent.

2.3. *General Equations for the Activities and the Partial Molar Enthalpies*

From the expressions for the integral quantities [Eqs. (7) and (8)] the equations for the compositional dependence of the partial molar quantities can be derived by following the method used previously by *Chang*[5]. For the activities one obtains:

$$\begin{aligned} \ln\left(\frac{a_i}{a_{i,0}}\right) = & \frac{\beta}{2}(\psi_0 - \psi) + \frac{1}{2} \ln \frac{\phi + \psi}{\phi_0 + \psi_0} - \\ & - \varepsilon_i \left[2\beta(z - \alpha) - \ln \frac{(1 - 2\chi - 2z)}{(1 - 2\alpha)(\chi + z)} \right] + \frac{3\eta}{4 - 3\eta} \beta \chi (\chi + 2\varepsilon_i), \end{aligned} \tag{9}$$

and for the partial molar enthalpies:

$$\begin{aligned} \frac{\Delta \overline{H}_i - \Delta \overline{H}_{i,0}}{RT} = \beta \Bigg\{ & 2(z^2 - \alpha^2) - (z - \alpha) + \left(\frac{\mathrm{d}z}{\mathrm{d}\chi}\right) \chi \phi - \\ & - \varepsilon_i \left[2z - \left(\frac{\mathrm{d}z}{\mathrm{d}\chi}\right) \phi - \frac{1}{2} \right] \Bigg\} + \frac{3\eta}{4 - 3\eta} \beta \chi (\chi + 2\varepsilon_i), \end{aligned} \tag{10}$$

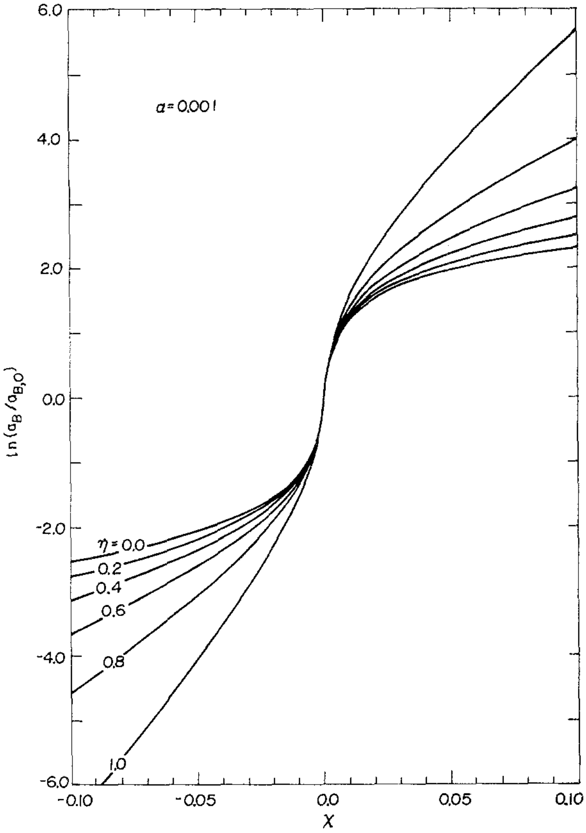

Fig. 1. Activity of the component **B** as a function of composition for $\alpha = 1 \times 10^{-3}$ and different η-values between 0.0 and 1.0 according to Eq. (9)

where

$$\beta = \frac{2}{1-4\alpha} \ln \frac{2\alpha}{1-2\alpha}\,; \tag{11}$$

$$\phi = 1 - 2\chi - 4z \text{ and } \phi_0 = 1 - 4\alpha; \tag{12}$$

$$\psi = 4z(\chi + z) \text{ and } \psi_0 = 4\alpha^2. \tag{13}$$

For $i = 1$ (component **A**) $\varepsilon_i = +\tfrac{1}{2}$ and for $i = 2$ (component **B**) $\varepsilon_i = -\tfrac{1}{2}$; $a_{i,0}$ and $\Delta \overline{H}_{i,0}$ are the activity and the partial molar enthalpy of the component i at the stoichiometric composition. As can be seen, for $\eta = 0$, i.e., if the interactions between second-nearest neighbors are neglected, Eqs. (9) and (10) reduce to Eqs. (71) and (85b) by *Chang*[5], resp.

Figs. 1 and 2 show the curves for the activity and the partial molar enthalpy of component **B** as a function of χ for $\alpha = 1 \times 10^{-3}$ at different η-values between 0.0 and 1.0; they were calculated from Eqs. (9) and (10). The influence of the parameters α and η on these curves can be distinguished very clearly: the shape of the curves near the stoichiometric composition is determined mainly by α, whereas their slope at larger deviations from stoichiometry is controlled by η.

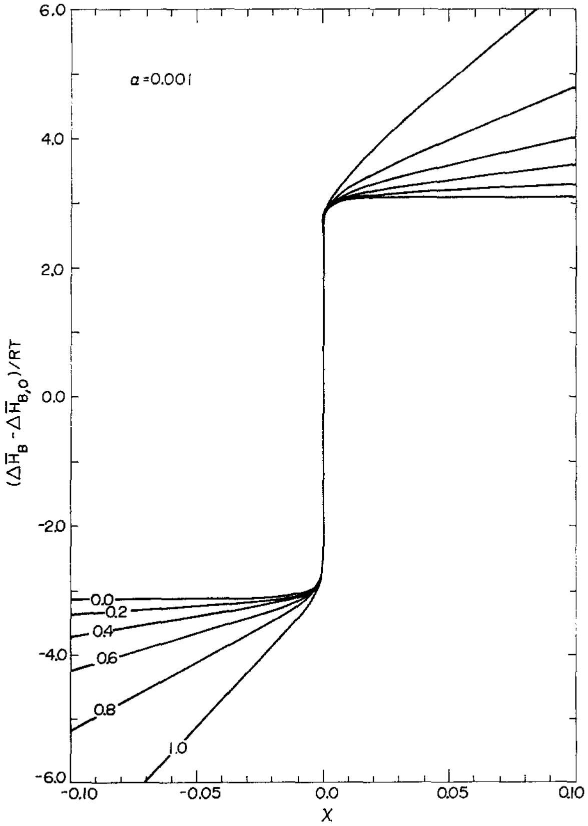

Fig. 2. Partial molar enthalpy of the component **B** as a function of composition for $\alpha = 1 \times 10^{-3}$ and different η-values between 0.0 and 1.0 according to Eq. (10)

2.4. *Simplified Equations for the Activities and the Partial Molar Enthalpies*

The expressions for the activities and the partial molar enthalpies can be simplified considerably. Similar to the manner demonstrated by *Neumann* et al.[6] for phases with the triple-defect B 2 structure, one can neglect the terms z^2 and χz compared to z in the equation for the integral enthalpy, Eq. (7):

$$H = \frac{N}{2}[8(4-3\eta)(-z)\,V_{\mathbf{AB}} - 24\eta\chi^2\,V_{\mathbf{AB}} + 4\,(2-4\chi)\,H_{\mathbf{AB}} + \\ + 12\chi\,H'_{\mathbf{AB}} + 3\,(1-4\chi)\,H'_{\mathbf{AA}} + 16\chi\,H_{\mathbf{BB}} + 3H'_{\mathbf{BB}}]\,. \tag{14}$$

By combining Eqs. (14) and (8), an expression for the free enthalpy G can be obtained; minimization of the free enthalpy with respect to z yields:

$$4N\,(4-3\eta)\,V_{\mathbf{AB}} = RT\ln\frac{4z\,(z+\chi)}{(1-2z)\,[1-2\,(\chi+z)]}\,. \tag{15}$$

For $\chi = 0$ $(z = \alpha)$, this expression reduces to:

$$4N\,(4-3\eta)\,V_{\mathbf{AB}} = RT\ln\frac{4\alpha^2}{(1-2\alpha)^2}\,. \tag{16}$$

By equating the right-hand sides of (15) and (16) one obtains a relationship between z, χ, and α which is a simplified form of Eq. (28) by *Chang*[5]:

$$\frac{z\,(z+\chi)}{(1-2z)\,[1-2\,(\chi+z)]} = \frac{\alpha^2}{(1-2\alpha)^2}\,. \tag{17}$$

For small concentrations of substitutional defects, i.e. $z \ll 1$, $(z + \chi) \ll 1$, and $\alpha \ll 1$, Eq. (17) can be simplified:

$$z\,(z+\chi) = \alpha^2 \tag{18a}$$

or

$$z = -\frac{\chi}{2} + \frac{\sqrt{\chi^2 + 4\alpha^2}}{2}\,. \tag{18b}$$

Eq. (18a) represents the ideal mass action law for the formation of substitutional defects. On the other hand, it is identical with the so called "One-and-Half Approximation" obtained by *Chang* and coworkers[1–5] from the condition $\psi = \psi_0$ [see Eq. (13)].

The application of the well known relationships between integral and partial molar quantities in combination with Eqs. (17) and (18) leads to simplified expressions for the thermodynamic activities and the partial molar enthalpies. For the activities one can derive:

$$\ln\frac{a_i}{a_{i,\,0}} = \varepsilon_i\ln\frac{z\,(1-2\alpha)}{\alpha\,(1-2z)} + \frac{3\eta}{4-3\eta}\,\chi\,(\chi+2\,\varepsilon_i)\,2\ln 2\alpha, \tag{19}$$

where the factor 2 ln 2α is obtained by simplification of the term

$\ln [4\,\alpha^2/(1 - 2\,\alpha)^2]$ for $\alpha \leqslant 1$. Eq. (19) is equivalent to *Chang's* "One-and-Half Approximation" for the activities, when $\eta = 0$.

On the other hand, for $\eta = 0$, $(1 - 2\,z) \approx 1$, and $(1 - 2\,\alpha) \approx 1$, Eq. (19) reduces to:

$$\ln \frac{a_i}{a_{i,\,0}} = \varepsilon_i \ln \frac{z}{\alpha}\,. \qquad (20)$$

The similarity between (20) and the so-called "Approximation II" of *Neumann* et al. for triple-defect B 2 phases is evident [Eqs. (15) and (16) in Ref. [6]].

For the partial molar enthalpies the following equation is obtained:

$$\frac{\Delta \bar{H}_i - \Delta \bar{H}_{i,\,0}}{RT} = \left[2\,\alpha - \frac{4\,\alpha^2 - \varepsilon_i\,\chi}{2\,z + \chi} + \frac{3\,\eta}{4 - 3\,\eta}\,2\,\chi\,(\chi + 2\,\varepsilon_i)\right] \ln 2\,\alpha. \qquad (21)$$

For $\eta = 0$ Eqs. (21) is identical with *Chang's* "One-and-Half Approximation" for the partial molar enthalpies[5], if β, which is defined in Eq. (11), is replaced by its simplified form $2 \ln 2\,\alpha$.

For reasonably small α-values ($\alpha < 1 \times 10^{-2}$), the curves calculated from the simplified equations (19) and (21) for the activities and the partial molar enthalpies, resp., agree well with those calculated from the corresponding general equations (9) and (10).

3. Comparison with Experimental Data

Using the experimental data reported in the literature, the following intermetallic phases with substitutional B 2 structure were evaluated with respect to α and η: β'-AuZn[12], β'-AuCd[13, 14], β'-AgMg[15], and β'-NiZn[7, 8]. In the case of β'-AuCd and β'-NiZn, the data from two different studies were combined for the evaluation. Although the general equations (9) and (10) were used for the determination of the parameters α and η, the approximations given by Eqs. (19) and (21) yield virtually the same results except for β'-AgMg, which exhibits a rather high degree of disorder ($\alpha = 2.5 \times 10^{-2}$). The evaluation is demonstrated for β'-AuZn, where the discrepancies between the theoretical curve and experimental activities at larger deviations from stoichiometry had been found to be the most significant. Fig. 3 shows the zinc-activities by *Pemsler* and *Rapperport*[12] together with the curve calculated from Eq. (9) with $\alpha = 1.1 \times 10^{-3}$ and $\eta = 0.5$; also shown in the figure is the curve previously calculated by *Kou* and *Chang*[9] with $\alpha = 7 \times 10^{-4}$, assuming $\eta = 0$. It can be seen clearly that the agreement is much better when interactions between second-nearest neighbors are taken into account. In Fig. 4 the experimental $\Delta \bar{H}_{\mathrm{Zn}}$-data for β'-AuZn by *Pemsler* and *Rapperport*[12] are compared with the theoretical curve calculated from Eq. (10) using the values for α and η found from the activity curve. Although the partial molar enthalpies obtained from activity measurements as a function of temperature are generally less reliable than the activities themselves, the agreement between theory and experiment is also quite good.

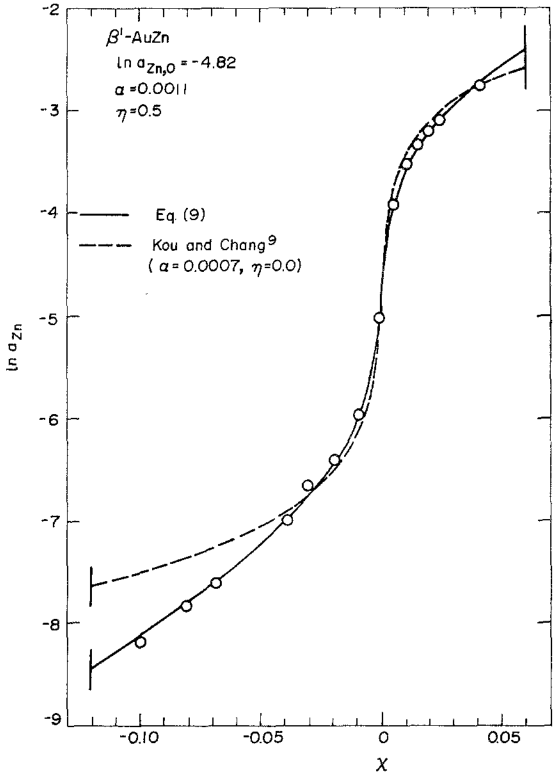

Fig. 3. Activity of zinc in β'-AuZn at 700 K; ○ = experimental data by *Pemsler* and *Rapperport*[12]

The α- and η-values obtained from the evaluation of the four phases with substitutional B 2 structure are summarized in Table 2 together with the temperatures for which the evaluations were carried out. It is believed that the η-values given are accurate within ± 0.1, although the scatter of the experimental data for activities and partial molar enthalpies is in most systems quite large with respect to the refinement of the theoretical model. Table 2 contains furthermore the enthalpies of formation of the phases referred to the solid elements as standard state, the α-values determined previously by *Chang* and co-workers[1, 5, 8, 9] neglecting second-nearest neighbor interactions and those reported by *Libowitz*[17].

As pointed out before, the shape of the activity curves near the stoichiometric composition is mainly determined by the disorder parameter α, and it is little affected by the introduction of second-nearest neighbor interactions. Consequently, there is only a slight difference between the disorder parameters calculated with or without second-nearest neighbor interactions.

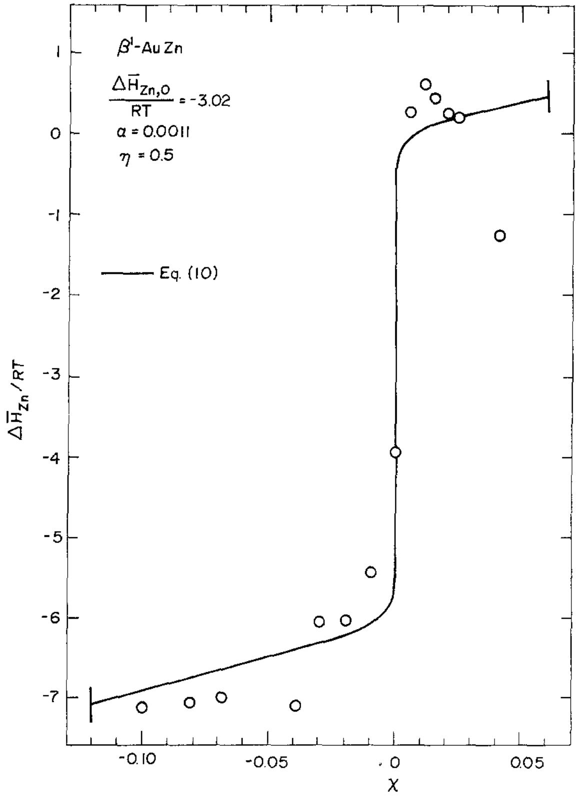

Fig. 4. Partial molar enthalpy of zinc in β'-AuZn; ○ = experimental data by *Pemsler* and *Rapperport*[12]

4. Relationship Between the Model Parameters and the Enthalpy of Formation

The relationship between the enthalpy of formation ΔH_f and the disorder parameter α for B 2 phases has recently been discussed

Table 2. *Results of the Evaluation of B2 Phases Exhibiting Substitutional Defects*

Phase	$\frac{T}{\mathrm{K}}$	α (This study)	η	$\frac{-\Delta H_f}{\mathrm{kJ\,(g\text{-}atom)^{-1}}}$	α (*Chang* and co-workers)	α (*Libowitz*[17])
β′-AuZn	700	1.1×10^{-3}	0.5	25.8[16]	7.0×10^{-4} [5,9]	1.05×10^{-3}
β′-AgMg	873	2.5×10^{-2}	0.2	18.4[16]	2.1×10^{-2} [1,5]*	1.8×10^{-2}
β′-AuCd	700	2.8×10^{-3}	0.1	19.2[16]	2.6×10^{-3} [1,5]	2.5×10^{-3}
β′-NiZn	1100	9.0×10^{-3}	0.0	16.4 ($\pm$ 2.9)[8]	9.0×10^{-3} [8]	—

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* Converted from $\alpha_{773} = 1.4\times10^{-2}$ by means of Eq. (23): $T \ln (2\,\alpha) = \mathrm{const.}$

by the authors[18]. The following expression was obtained for phases exhibiting substitutional defects:

$$\frac{\Delta H_f}{RT} = \frac{1}{2} \ln (2\alpha), \tag{22}$$

which indicates a linear relationship between $\frac{\Delta H_f}{RT}$ and $\ln \alpha$. However, the experimental values of $\frac{\Delta H_f}{RT}$ are generally more negative than those calculated from Eq. (22); T is the temperature at which

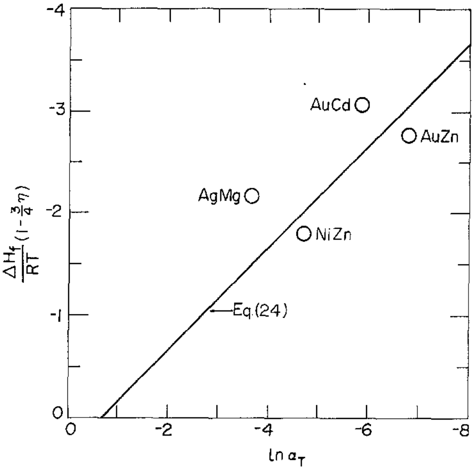

Fig. 5. Relationship between ΔH_f, α and η for B 2 phases with substitutional defects

α was determined. It appears that at least part of this systematic deviation can be explained as a consequence of the neglect of second-nearest neighbor interactions. For small values of α, Eq. (16) can be simplified:

$$4 N (4 - 3 \eta) V_{AB} = 2 RT \ln (2 \alpha). \tag{23}$$

If furthermore the term $4 N V_{AB}$ is identified with the enthalpy of formation ΔH_f, neglecting the difference in the crystal structures of the component elements for the sake of simplicity, one can write Eq. (23) as:

$$\frac{\Delta H_f}{RT}\left(1 - \frac{3}{4}\eta\right) = \frac{1}{2} \ln (2\alpha). \tag{24}$$

This relationship reduces to Eq. (22) for $\eta = 0$. Fig. 5 shows a comparison between the curve calculated from Eq. (24) and the experimental data for ΔH_f, α, and η from Table 2; as can be seen, the agreement is good and no systematic deviations are observed as it was the case for Eq. (22).

In addition, the authors also have presented a relationship between the enthalpy of formation of substitutional B 2 phases and their critical order-disorder temperature T_c at the stoichiometric composition[18]:

$$-\frac{\Delta H_f}{R} = T_c, \tag{25}$$

where T_c can either be determined experimentally or calculated by means of Eqs. (4) or (5) in Ref. [18]. This relationship corresponds to the well known *Bragg-Williams* expression. While the trend of the data was in general agreement with Eq. (25), a systematic deviation was observed. In fact the data were found to agree better with a relationship derived by means of the Monte Carlo technique:

$$-\frac{\Delta H_f}{R} = \frac{4}{3} T_c. \tag{26}$$

On the other hand, the inclusion of second-nearest neighbor interactions in the present work results in the following relationship:

$$-\frac{\Delta H_f}{R} = \frac{4}{4 - 3\eta} T_c. \tag{27}$$

A comparison of (26) and (27) shows that the two expressions are identical for a value of $\eta = 0.33$; for $\eta = 0$, i.e., neglecting the effect of second-nearest neighbors, (27) reduces to (25).

5. Discussion

Libowitz and *Lightstone*[19–22] have derived theoretical equations to describe the concentration dependence of the activities in ordered phases. Applying these equations, *Libowitz*[17] evaluated a number of B 2 phases, among them β′-AuZn, β′-AuCd, and β′-AgMg, which were also investigated here. His intrinsic defect concentrations, converted into the disorder parameter α, are listed in Table 2; the agreement with the values of α obtained in the present work is quite satisfactory. Interestingly, in the case of β′-AuZn, where *Chang's* original model[5] failed for even moderate deviations from stoichiometry, *Libowitz* had to assume interactions between defects on the gold-rich side of the homogeneity range, in order to obtain good agreement between his theoretical activity curve and the experimental data by *Pemsler* and

Rapperport[12]. However, the interactions between gold substitutional defects represent only part of all second-nearest neighbor interactions. It seems likely that the interaction energies for all possible pairs of second-nearest neighbors are of the same order of magnitude, so that, because of the small number of pairs of substitutional gold defects, their total contribution to the integral energy should be rather small. Therefore, it appears to be more reasonable to take all second-nearest neighbor interactions into account in the derivation of the theoretical equations, as was done in the present work.

Furthermore, *Libowitz* reported a discrepancy between the theoretical curve and the experimental data on the zinc-rich side of β′-AuZn, attributing it to possible ordering or clustering of defects. The inclusion of second-nearest neighbor interactions over the whole range of homogeneity results in an activity curve which describes the experimental data equally well on both sides of the stoichiometric composition without resorting to additional assumptions, as can be seen in Fig. 3.

When converting *Libowitz*'s notation to the one used here, namely, $n_{\mathrm{Au\,(Zn)}} \equiv 2\,z$, it can be shown from a comparison of his modified activity equation [Eq. (23) in Ref. [17]] and Eq. (19) that his defect-interaction energy $\xi_{\mathrm{Au\,(Zn)}}$ is equivalent to the term $-\,{}^1\!/_2\,\eta\,\Delta\,H_f$. The value of $\xi_{\mathrm{Au\,(Zn)}} = 8.8$ kJ/g-atom reported by *Libowitz*[17] is in reasonable agreement with the value of $-\,{}^1\!/_2\,\eta\,\Delta\,H_f = 6.5$ kJ/g-atom obtained in the present work.

Recently, *Inden*[23] estimated the hypothetical disorder temperature for β′-AuZn. Using this temperature and the known enthalpy of formation, the values for the interchange energies between first- and second-nearest neighbors were deduced; the ratio yields $\eta = 0.55$ which compares well with the value 0.5 given in Table 2.

While no quantitative explanation can be given for the rather significant variation of the parameter η for the different substitutional B 2 phases, there are indications that it might be related to the difference in their ionic character. For instance, β′-AuZn which has the highest η-value is characterized by the largest electronegativity difference between the elements (using the *Pauling*-type electronegativity values from *Allred*[24] as an approximation), and it also has the most negative enthalpy of formation. On the other hand, β′-NiZn with $\eta = 0$ exhibits one of the smallest electronegativity differences as well as one of the smallest enthalpies of formation.

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