BRAGG-WILLIAMS MODEL OF ORDERED B2, $L1_2$ and $L1_0$ TYPE BINARY INTERMETALLIC COMPOUNDS CONTAINING POINT DEFECTS

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CONTENT

Abstract

Ordered intermetallic compounds draw great interest at the present time because of both possible applications and fundamental scientific importance. The scientific interest is derived from the recognition that many intermetallics exhibit considerable ranges of nonstoichiometry which correspond to the presence of constitutional point defects which are temperature independent. Additional to these constitutional point defects thermally activated point defects can occur. The total defect structure (i.e. the types and the concentrations of the point defects) determines important properties of the intermetallic compounds (e.g. all diffusion dependent properties). Hence, for understanding and control of these properties a detailed knowledge of the defect structure in intermetallic compounds as function of composition and temperature within the homogeneity range of the compounds is a prerequisite. This thesis is aimed at formulating a model which can be used to calculating the ordering energy parameters ΔH_{AB} and $\Delta H_{B\square}$, and the concentration of vacancy (z) and the concentration of Antistructure Defect as a function of the composition parameter χ and the temperature T. The ordering energy is related to but different from the formation energy, because the former is the energy change from the disordered alloy AB to the ordered alloy AB, while the latter is the energy change from the pure metals A and B to the ordered AB. Having obtained the model parameters (note that these are ΔH_{ij} and ΔS_{ij} for the fitting of the vacancy concentration and h_{ij} and s_{ij} for the fitting of the thermodynamic properties, respectively), the temperature dependence of the vacancy concentration can also be determined.

CHAPTER ONE

Introduction

Now-a-days technology and metal are highly interrelated. When we say metals we mean crystals which are composed of a certain type of transition metal elements or compounds. There are metals composed of two or more type of atoms or alloys. Such type of metals is called intermetallic compounds. Intermetallic compounds, which are composed of two or more types of metallic elements or compounds, are our point of concern in this work.

As mentioned above, due to its high applicability metals are the subject of research from the old age up to now. In addition, intermetallic phases have been a subject of research for almost a century, and the idea that atomic ordering is responsible for their wide spectrum of properties is almost as old as the study of intermetallic phases [1]. Intermetallic compounds or ordered alloys have recently attracted much attention as structural materials for high temperature applications. Knowledge of thermal and structural defect formation is necessary for the use of these materials in technological applications [2]. Due to this intermetallics take a great attention of many scientists and researchers.

Through successive study scientists understood that one of the factors that determines the properties of intermetallics is the formation and concentration of point defects. In intermetallic compounds the most important point defects generally assumed are vacancies and antistructure atoms, i.e. atoms occupying a “wrong” site in the ordered crystal structure. In many cases, in elementary metals monovacancies dominate as point defects at least in some temperature range. On the other hand in intermetallic compounds more than one type of point defect can occur in order to maintain the ordered structure. Due to this, the experimental analysis of the defect structure of intermetallic compounds is difficult [3].

In general there are two methods in which scientists study the defect structure of intermetallic compounds. One is experimental while the other is theoretical. Each of them is discussed in the following paragraphs in a little more detail.

Regarding experimental method, different experimental techniques may be used for the determination of the various defect concentrations [4]. The absolute concentration of vacancy type defects can be determined by comparison of thermal expansion data measured by X-ray diffraction with experimental data measured by dilatometry (unit cell size change vs. volume/length change) [5]. Positron annihilation experiments [6] provide a sensitive means for the study of vacancies too. Other possible experiments for the determination of point defects involve intensity methods using X-ray diffraction [7], field ion microscopy [8], magnetic susceptibility [2] and Mössbauer measurements [9]. Despite the large number of available experimental methods, many of these methods provide only information on ”effective” defect properties (i.e. they respond to the total defect structure) and often they can be applied only in a certain defect concentration window.

On the other hand the theoretical analysis of the defect structure of intermetallic compounds may be subdivided into two groups: statistical methods associated with *ab initio* calculations and statistical methods associated with *experimentally* measured data [10]. In the *ab initio* statistical methods [11] an expression for the grand canonical potential is minimized with respect to the defect concentrations. The input parameters are defect energy parameters which are obtained by *ab initio* calculations. The defect formation entropies are neglected. In the second group of statistical methods [12] an expression for the free energy as a function of the various defect concentrations is minimized with respect to the defect concentrations. The input parameters appearing in the expression for the free energy are determined by fitting the theoretical expressions to experimental data. In both (types of statistical) methods, i.e. using *ab initio* calculations or experimental data, it is assumed that the input parameters are independent of the defect concentrations and of the temperature.

Some of the approaches of the statistical methods require certain type of input parameters different from the others to determine the defect concentration. In the approaches based on the Bragg-Williams concept the input parameters are the energies of interaction of neighbouring atoms and the corresponding entropy parameters [13]. In the approaches based on the Wagner-Schottky concept [14] the input parameters are the concentrations of antisite atoms on each of the sublattices and the total vacancy concentration (combining the sublattices) at the stoichiometric composition and at the considered temperature (i.e. in this case the input

parameters include information on both the energy and the entropy). Other possible input parameters in Wagner-Schottky approach are the enthalpies of formation of the four types of point defects (neglecting defect formation entropies) [15]. Of the statistical methods, the Bragg-Williams approach is an easily applicable formalism that leads to accurate predictions concerning thermodynamic data as well as defect concentrations [16].

A number of models have been developed for the description of the thermodynamic properties of B2, $L1_2$ and $L1_0$ phases usually using a Bragg–Williams (B–W) or Wagner–Schottky (W–S) formalism [17]. These models are useful for making predictions of defect concentrations and for providing the thermodynamic description of the phase for computational thermodynamics databases. An excellent review on this topic was written by Chang and Neumann [18]. Since then, additional experimental data have become available, in particular, enthalpy of formation, lattice parameter, and defect concentrations [19].

The present thesis reports such an extension of the model for a binary A_mB_n compound that is composed of two sublattices. A pair interaction model applying the Bragg-Williams approach is presented. The formalism is given in a general form for binary ordered compounds with B2, $L1_2$ and $L1_0$ crystal structures considering all possible types of point defects. With this general model the essential equations for three common ordered structures (B2, $L1_0$ and $L1_2$) can be easily derived.

Three of the most common superlattices occurring in binary intermetallic phases are the B2 type (or CsCl type), the $L1_0$ type (or AuCuI type) and the $L1_2$ type (or Au_3CuI type). As shown in Figure 1.1(a), the ordered structure of the B2-type has two atoms per unit cell with one kind (say, B atom) occupying the body-centered position and the other (say, A atom) occupying the corner position. The symmetry is no longer of body-centered cubic but one of simple cubic with each lattice point associated with two different atoms. The structure may also be considered as consisting of two simple cubic sublattices interpenetrating each other. The $L1_2$ type ordered structure as shown in Figure 1.1 (b) is similar to that of B2 type. The only difference between them is in the ratio of A atoms to B atoms. In the case of B2 the ratio is 1:1 while in the case of $L1_2$ the ratio is 1:3. Accordingly, in the $L1_2$ type ordered structure all A atoms are located on the

corner positions while all B atoms are located on the face-centered positions. The symmetry in $L1_2$ type becomes one of simple cubic having four atoms associated with each lattice point.

The face-centered tetragonal $L1_0$ type (AuCuI type) superlattice as shown in Figure 1.1 (c) is also one of the ordered phase. However, in this case the ratio of A to B atoms is 1:1 with the two different kinds of atoms occupying the alternate (001) layers, resulting in a tetragonal distortion of the lattice.

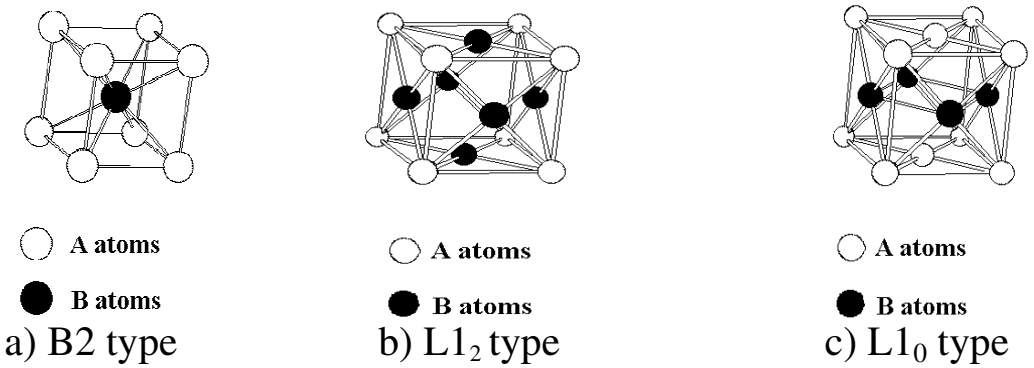

Figure 1.1: Structures of three common superlattices in binary intermetallic phases

From the foregoing discussion, it is obvious that perfectly ordered structures are possible only at the simple atomic ratios of 1:1 or 3:1 for the three superlattices considered. Deviations from the simple atomic ratios will result in the formation of lattice disorder introduced by point defects.

There are a large number of binary and ternary intermetallic compounds with the B2 (or CsCl) structure, many of which exist over substantial composition ranges [20]. One of the interesting aspects of the B2 structure is the existence of constitutional crystal defects when the composition deviates from the stoichiometric composition. In the fully ordered stoichiometric compound, one type of atom occupies the α-sublattice while the other type of atom occupies the β-sublattice. This occurs only at 0 K, but at finite temperatures thermal defects are present in increasing number as the temperature is increased. When there are no longer equal numbers of the two atoms the structure must introduce some type of atomic defect to maintain the crystal structure.

While several types of defects are possible, experience has shown that the most common defects in the case of B2 type FeAl are TM (Transition metals such as Fe) antistructure atoms on the Al-sublattice for composition deviations to the TM side and vacancies on the TM sublattice when there is an Al excess. At stoichiometry, it is possible for intermetallic compounds to have TM antistructure atoms on the Al-sublattice with two vacancies on the TM sublattice to maintain the equality of lattice sites, so-called triple defects [21]. Deviations from stoichiometry are accommodated by TM vacancies in TM-deficient alloys and by TM antisite atoms in TM-rich alloys. However, additional point-defect disorder has been observed even in well-annealed samples of FeAl, for example by X-ray diffraction [22]. Such disorder is a consequence of a low enthalpy of formation of thermal defects and a high enthalpy of migration of vacancies, making it difficult to reach thermal equilibrium at low temperature. In FeAl the disorder is believed to involve the same defects that accommodate deviations from stiochiometry, that is, Fe-vacancies, V_{Fe}, and Fe-antisite atoms, Fe_{Al} [2]. Other elementary point defects that have not been reported for annealed samples include the Al-antisite atom, Al_{Fe}, and Al-vacancy, V_{Al}.

A subset of the B2 compounds, the aluminides, where one of the major components is Al and the other is generally a TM element, are of interest for use in high-temperature structural applications because of their low densities, high melting points, and oxidation resistance [23]. Iron aluminides represent an intriguing class of materials; they offer a good combination of mechanical properties, specific weight/strength ratio, corrosion (and oxidation) resistance and low raw material cost. These properties make them potential candidates for the substitution of stainless steel in applications at moderate to high temperature. It is well known that upon rapid quenching from elevated temperatures iron aluminides retain a high concentration of thermal vacancies which when frozen increase their yield strength and hardness at room temperature [24]. Despite these useful properties, the aluminides still present considerable challenges for such applications, in particular, they exhibit poor room temperature ductility and creep resistance [19].

Intermetallic compounds showing high stability of superstructure are promising technological materials. As their attractive properties follow mostly from a high degree of long-range atomic order (LRO), knowledge of ordering kinetics in these systems is crucial.

LRO is an essential factor responsible for attractive technological properties of many intermetallic compounds. Effective production of these materials involves, therefore, specific procedures (e.g. thermal treatments) aiming at a generation of particular atomic configuration in their crystalline lattice. Physically, the configurations form according to the rules of diffusional kinetics, among which ordering kinetics plays a principal role. The process has been investigated for several decades including a study of one of its specific aspects: so-called "order–order" kinetics. The "order–order" kinetics, a relaxation of atomic configuration following an abrupt temperature variation within the domain of LRO (i.e. below the "order–disorder" transformation) is a process controlled by atomic migration, which, however, occurs under non-stationary conditions. This fact makes that, despite showing the same microscopic mechanism as steady-state diffusion (i.e. predominantly atomic jumps to the neighbouring vacancies), "order–order" kinetics may be characterised by different values of e.g. activation energy. Consequently, when designing technology of intermetallic materials, not only diffusion characteristics, but also ordering kinetics should be referred to.

The development of new, more ductile, intermetallic alloys depends on a thorough understanding of their properties implicating a better comprehension of the properties and behavior of defects in these materials. Experimental as well as theoretical studies suggest that intermetallics present complex point defects, especially triple defects. It is expected that the concentration of vacancies can be strongly changed in the intermetallics with the variation of heat and mechanical treatment, together with the composition modification of the intermetallics by transition metal ternary additives [25].

The defect equilibrium as function of composition and temperature at constant pressure may be described by statistical thermodynamic models [23]. The validity of a model for a particular phase can be tested by comparing measured and calculated data for the Gibbs free energies of formation as function of composition. Here notice that the experimental values for the Gibbs free energy of formation have to be known with sufficient accuracy.

Theoretical method provides an evaluation of the different statistical methods, i.e. employing either *ab initio* calculations or applying the Bragg-Williams or Wagner-Schottky approaches. The discussion about applicability and outcome of pair interaction models based on

the Bragg-Williams approach emphasizes its role as an easily utilized and powerful tool in the determination of defect concentrations from thermodynamic properties.

In the work of J. Breuer [16] a generalized Bragg-Williams model for ternary ordered intermetallic compounds having B2 and $L1_0$ crystal structures incorporating any type of defect was presented. But the model has not been extended to work for $L1_2$ ordered crystal structure. Even though the work says the generalized model works also for $L1_2$, the formulation started by fixing values used for B2 and $L1_0$. On the other hand in another paper a model for binary B2 type intermetallic compounds is derived for a limited number of defects [23]. Both of these works are incomplete and motivated us as the starting point for our thesis work.

Applying a Bragg-Williams approach, the present study provides a method to extract the description of the interaction between pairs of species in the compounds (atoms/atoms and atoms/defects), the enthalpy of formation, the Gibbs free energy as well as the defect structure of the ordered binary intermetallic compounds for the B2, $L1_2$ and $L1_0$ types. The work formulates a procedure of how to search for a right defect concentration to predict the physical parameters. To mention a few, first, a general form of pair interaction model of Bragg-Williams for binary ordered compounds for B2, $L1_2$ and $L1_0$ type structures is designed. And then a model is specifically derived for B2 type binary intermetallic compounds containing hybrid (four) defect. In the application of the model on B2 type binary intermetallic compounds, all the important equations are used to self-consistently match with the experimental data to determine some parameters which has contribution on the determination of the properties of the intermetallic compounds.

The rest of the thesis is organized as follows. In Chapter two a generalized Bragg-Williams model for binary ordered intermetallic compounds containing certain types of point defect is derived. In Chapter three a specific model appropriate for B2 type binary intermetallic compounds suitable for all types of point defects is derived. In Chapter four discussion and conclusion is presented. In general in this thesis we derived a generalized Bragg-Williams model for B2, $L1_2$ and $L1_0$ type binary intermetallic compounds containing any type of point defects. In addition to that we derived a simpilified model for B2 type binary intermetallic compounds containing any type of point defects. Here it is important to note that there are works in which a

Bragg-Williams model for B2 binary intermetallic compounds was used. But those works cannot be used for any type of defects while the present work can be used for all types of point defects. We know of no previous work where this is done. Hence, to the best of our knowledge the work presented in this thesis has not been done previously by others.

CHAPTER TWO

Bragg-Williams model approach for binary ordered compounds

2.1 The Model

In an ordered intermetallic compounds vacancy formation still remains unclear. One unsolved but central problem in intermetallics is how to understand why there exist a variety of different types of intermetallic compounds which exhibit very different vacancy concentrations with vastly different temperature dependences [26].

The model we want to address is a generalized Bragg-Williams model for binary ordered intermetallic compounds having a crystal structure composed of two sublattices. Due to this we can apply this model for binary ordered intermetallic compounds having a structure composed of two sublattices like B2, $L1_2$ and $L1_0$ to find thermodynamic data such as defect concentrations. In this statistical thermodynamic model (for a survey, see [12]) an expression for the free energy is minimized with respect to the various defect concentrations. The energies of interaction of neighbouring atoms (H) and the corresponding entropy of interaction of neighbouring atoms including configurational entropy (S) appearing in the expression for the Gibbs free energy (G) are determined by fitting the theoretical expressions to experimental data. The relation between these three physical quantities is given by

$$G = H - TS, \qquad (2.1)$$

where T is the temperature of interaction of neighbouring atoms.

In order to describe the number of atoms and defects in each sublattice, we first define the parameters characterizing them and this will be done in the next section.

2.1.1 Assumptions and their relations

To describe the point defect structure of the binary ordered intermetallic compounds having the structure mentioned above, consider the following definitions and assumptions which one usually uses [26].

1. A binary compound whose chemical formula is A_mB_n .

2. N_I^{δ}designates the number of I (=A, B, vacancy (□)) species on the δ (= α, β) sublattice. For example, N_A^{α} is the number of A atoms on the α sublattice.

3. The total numbers of A and B atoms in the crystal are N_A and N_B, respectively. N denotes the constant total number of atoms (here one mole of atoms is considered, so N = Avogadro's number): $N = N_A + N_B$.

4. The composition variable (χ) specifies the overall composition of the binary system $\chi = \frac{N_B}{N} - \frac{n}{m+n} = -\frac{N_A}{N} + \frac{m}{m+n}$.

5. The defects considered are A atoms on the β sublattice (numbers:N_A^{β}), B atoms on α sublattice (number:N_B^{α}), vacancies on α sublattice (number:$N_{\square}^{\alpha}$) and vacancies on the β sublattice (number:$N_{\square}^{\beta}$).

6. In the defect free ideal crystal, which can only exist at the stoichiometric composition at 0 K, all A atoms occupy all α sublattice sites, while all B atoms occupy all β sublattice sites. The crystal consists of mα sites and nβ sites. The total number of sites N_s, $N_s = N + N_{\square} = N + N_{\square}^{\alpha} + N_{\square}^{\beta}$, is variable.

7. The concentration of A atoms on the β sublattice is defined as $y_A \equiv \frac{N_A^{\beta}}{N}$ and the concentration of B atoms on the α sublattice is defined as $y_B \equiv \frac{N_B^{\alpha}}{N}$, respectively. The vacancy concentration on the α sublattice is defined as $z_{\alpha} \equiv \frac{N_{\square}^{\alpha}}{N}$ and the vacancy concentration on the β sublattice is defined as $z_{\beta} \equiv \frac{N_{\square}^{\beta}}{N}$.

8. The total concentration of vacancies, z, is given by $z = z_\alpha + z_\beta$.

9. For small deviations from the stoichiometric composition the concentration of defects is small. Then it can be supposed that the defects are randomly distributed and do not interact. Therefore, enthalpy and entropy contributions containing z, z_α, z_β, y_A, y_B and/or χ in the second or higher power are neglected. The approximation $\frac{1}{1+z} \approx 1 - z$ is applied.

The numbers of atoms and vacancies on the α and β sublattices can be expressed interms of N, y_A, y_B, z_α, z_β, z and χ. These expressions are shown in Table 2.1.

Table 2.1: Numbers of atoms and vacancies on the α and β sublattices.

	α-site	β-site	Total number of sites
A atoms	$N_A^\alpha = \left(\frac{m}{m+n}\right) N\left[1 - (\chi + y_A)\left(\frac{m+n}{m}\right)\right]$	$N_A^\beta = \left(\frac{n}{m+n}\right) N y_A \left(\frac{m+n}{n}\right)$	$N_A = \left(\frac{m}{m+n} - \chi\right) N$
B atoms	$N_B^\alpha = \left(\frac{m}{m+n}\right) N y_B \left(\frac{m+n}{m}\right)$	$N_B^\beta = \left(\frac{n}{m+n}\right) N\left[1 - (y_B - \chi)\left(\frac{m+n}{n}\right)\right]$	$N_B = \left(\chi + \frac{n}{m+n}\right) N$
Vacancies	$N_\square^\alpha = \left(\frac{m}{m+n}\right) N z_\alpha \left(\frac{m+n}{m}\right)$	$N_\square^\beta = \left(\frac{n}{m+n}\right) N z_\beta \left(\frac{m+n}{n}\right)$	$N_\square = N(z_\alpha + z_\beta)$
Total sites	$N^\alpha = \left(\frac{m}{m+n}\right) N_s = \left(\frac{m}{m+n}\right) N(1+z)$	$N^\beta = \left(\frac{n}{m+n}\right) N_s = \left(\frac{n}{m+n}\right) N(1+z)$	$N_s = N(1+z)$

From the above table and assumption 6 we can write the expressions for z_α and z_β as

$$z_\alpha = \left(\frac{m}{m+n}\right) z + \chi + y_A - y_B, \qquad (2.2a)$$

and

$$z_\beta = \left(\frac{n}{m+n}\right) z - \chi - y_A + y_B, \qquad (2.2b)$$

respectively.

The relationship between the four kinds of point defects can be obtained by subtracting Eq. (2.2b) from Eq. (2.2a):

$$z_\alpha - z_\beta = \left(\frac{m-n}{m+n}\right) z + 2y_A - 2y_B + 2\chi. \qquad (2.3)$$

The independent variables in Eq. (2.2a) and Eq. (2.2b) are only three out of the five unknown concentrations z_α, z_β, z, y_A and y_B. Since the total vacancy concentration z and the concentration of antistructure atoms on both sublattices, y_A and y_B, seem to be the quantities that can most easily be obtained experimentally, one can choose these three concentrations (z, y_A, y_B) as independent variables.

With the partition of atoms and defects shown in Table 2.1, we can calculate the number of six kinds of nearest-neighbour atomic bonds, AA, BB, AB, B□ (□ means vacancy), A□ and □□, by using the mean-field approximation. Assuming that $x \ll 1$, $z_\alpha \ll 1$, $z_\beta \ll 1$, $y_\mathrm{A} \ll 1$ and $y_\mathrm{B} \ll 1$, we can neglect terms higher than first order of these quantities during calculation. The number of these atomic bonds is thus given by

$$n_{AA} = Z\left(N_A^\beta C_A^\alpha\right) = Z\left(\frac{n}{m+n}\right) N y_A \left(\frac{m+n}{n}\right)\left[1 - (\chi + y_A)\left(\frac{m+n}{m}\right)\right] = NZy_A, \quad (2.4a)$$

$$n_{BB} = Z\left(N_B^\alpha C_B^\beta\right) = Z\left(\frac{m}{m+n}\right) N y_B \left(\frac{m+n}{m}\right)\left[1 - (y_B - \chi)\left(\frac{m+n}{n}\right)\right] = NZy_B, \quad (2.4b)$$

$$n_{AB} = Z\left(N_A^\alpha C_B^\beta + N_B^\alpha C_A^\beta\right) = NZ\left[\left(\frac{m}{m+n}\right) - y_A - \chi - y_B\left(\frac{m}{n}\right) + \chi\left(\frac{m}{n}\right) - z\right], \quad (2.4c)$$

$$n_{A\square} = Z\left(N_\square^\beta C_A^\alpha + N_A^\beta C_\square^\alpha\right) = NZz_\beta, \quad (2.4d)$$

$$n_{B\square} = Z\left(N_\square^\alpha C_B^\beta + N_B^\alpha C_\square^\beta\right) = NZz_\alpha, \quad (2.4e)$$

$$n_{\square\square} = Z\left(N_\square^\beta C_\square^\alpha\right) = Z\left[\left(\frac{n}{m+n}\right) N z_\beta \left(\frac{m+n}{n}\right) z_\alpha \left(\frac{m+n}{m}\right)\right] = 0. \quad (2.4f)$$

Note that C_I^δ(I = A, B, □; δ = α, β) designates the concentration of I in the δ sublattice and is defined by the number of I in the δ sublattice divided by the total site number of the δ sublattice: $N^\delta = (N/2)(1 + z)$. Z is the coordination number of nearest-neighbour atomic bond for B2, $L1_2$ or $L1_0$ structure.

Similarly, we can calculate the number of next-nearest-neighbour atomic bonds interaction, AA, BB, AB, B□ (□ means vacancy), A□ and □□, by using the mean field approximation.

$$n'_{AA} = Z'\left(N_A^{\alpha} C_A^{\alpha} + N_A^{\beta} C_A^{\beta}\right) = NZ'\left(\frac{m}{m+n}\right)\left[1 - 2(\chi + y_A)\left(\frac{m+n}{m}\right) - z\right], \quad (2.5a)$$

$$n'_{BB} = Z'\left(N_B^{\alpha} C_B^{\alpha} + N_B^{\beta} C_B^{\beta}\right) = NZ'\left(\frac{n}{m+n}\right)\left[1 - 2(y_B - \chi)\left(\frac{m+n}{n}\right) - z\right], \quad (2.5b)$$

$$n'_{AB} = Z'\left(N_A^{\alpha} C_B^{\alpha} + N_B^{\beta} C_A^{\beta}\right) = NZ'(y_B + y_A), \quad (2.5c)$$

$$n'_{A\square} = Z'\left(N_{\square}^{\alpha} C_A^{\alpha} + N_A^{\beta} C_{\square}^{\beta}\right) = NZ'\left(\frac{m}{m+n}\right) z_{\alpha}\left(\frac{m+n}{m}\right) = NZ' z_{\alpha}, \quad (2.5d)$$

$$n'_{B\square} = Z'\left(N_{\square}^{\alpha} C_B^{\alpha} + N_B^{\beta} C_{\square}^{\beta}\right) = NZ'\left(\frac{n}{m+n}\right) z_{\beta}\left(\frac{m+n}{n}\right) = NZ' z_{\beta}, \quad (2.5e)$$

$$n'_{\square\square} = Z'\left(N_{\square}^{\alpha} C_{\square}^{\alpha} + N_{\square}^{\beta} C_{\square}^{\beta}\right) = 0. \quad (2.5f)$$

Here Z' is the coordination number of next-nearest-neighbour atomic bond of B2, $L1_2$ or $L1_0$ structure.

2.1.2 Dependence of the defect concentration on composition and temperature

2.1.2.1 Gibbs free energy

The next step in the development of the model is the formulation of the Gibbs free energy (G). According to the Bragg-Williams approach, the Gibbs free energy will be formulated by considering the interaction of only pairs of atoms (a vacancy is considered as an "atom"). The interaction enthalpy and the vibrational or phononical entropy of each type of bond between pairs of atoms are assumed to be independent of composition and temperature.

Consider nearest- and next-nearest-neighbour interactions for the enthalpy of the intermetallic compound. The general expression for the enthalpy then is

$$H = \sum_{ij} n_{ij} h_{ij} + \sum_{ij} n'_{ij} h'_{ij}. \quad (2.6)$$

where n_{ij} is the number of nearest-neighbour pairs i - j and h_{ij} is the corresponding interaction enthalpy (i and j can be A or B atoms, or vacancies □), and the analogous terms for the next-nearest-neighbour interaction are represented by n'_{ij} and h'_{ij}.

Let AA, BB, AB, B□, A□ and □□ bonds have bond energies h_{AA}, h_{BB}, h_{AB}, $h_{\mathrm{B}\square}$, $h_{\mathrm{A}\square}$ and $h_{\square\square}$, respectively, for nearest-neighbour atoms interaction and h'_{AA}, h'_{BB}, h'_{AB}, $h'_{B\square}$, $h'_{A\square}$ and $h'_{\square\square}$ for next-nearest-neighbour atoms interaction. We are then able to express the internal energy H in terms of defect concentrations so that

$$H = n_{AA}h_{AA} + n_{BB}h_{BB} + n_{AB}h_{\mathrm{AB}} + n_{B\square}h_{\mathrm{B}\square} + n_{A\square}h_{\mathrm{A}\square} + n_{\square\square}h_{\square\square} + n'_{AA}h'_{AA} + n'_{BB}h'_{BB} + n'_{AB}h'_{AB} + n'_{B\square}h'_{B\square} + n'_{A\square}h'_{A\square} + n'_{\square\square}h'_{\square\square}. \quad (2.7)$$

The number of atomic bonds (n_{ij} and n'_{ij}) are derived on the basis of the relations given in Table 2.1 for the numbers of atoms and vacancies on the α and β sublattices. By considering the coordination number Z for nearest-neighbour pairs and Z' for next-nearest-neighbour pairs, the following expression is obtained for the enthalpy H:

$$\begin{aligned}\mathrm{H} = {} & NZ\left\{\left(\frac{n}{m+n}\right)y_A\left(\frac{m+n}{n}\right)h_{AA} + \left(\frac{m}{m+n}\right)\left[1 - y_A\left(\frac{m+n}{m}\right) - y_B\left(\frac{m+n}{n}\right) - \chi\left(\frac{n}{m} - \frac{m}{n}\right) + \right.\right. \\ & \left.\left. - z\right]h_{AB} + \left(\frac{n}{m+n}\right)z_\beta\left(\frac{m+n}{n}\right)h_{A\square} + \left(\frac{m}{m+n}\right)z_\alpha\left(\frac{m+n}{m}\right)h_{B\square} + \left(\frac{m}{m+n}\right)y_B\left(\frac{m+n}{m}\right)h_{BB}\right\} + \\ & + NZ'\left\{\left(\frac{m}{m+n}\right)\left[1 - 2(\chi + y_A)\left(\frac{m+n}{m}\right) - z\right]h'_{AA} + \right. \\ & + \left[\left(\frac{m+n}{m}\right)y_B\left(\frac{m}{m+n}\right) + \left(\frac{m+n}{n}\right)y_A\left(\frac{n}{m+n}\right)\right]h'_{AB} + \left(\frac{m+n}{m}\right)z_\alpha\left(\frac{m}{m+n}\right)h'_{A\square} + \\ & \left. + \left(\frac{m+n}{n}\right)z_\beta\left(\frac{n}{m+n}\right)h'_{B\square} + \left(\frac{n}{m+n}\right)\left[1 - 2(y_B - \chi)\left(\frac{m+n}{n}\right) - z\right]h'_{BB}\right\}. \end{aligned} \quad (2.8)$$

Note that the expression for H above (Eq. (2.8)) enables us to see the difference between our generalized model and that of J. Breuer *et al*. [16]. In fact their work was for ternary atoms but it can be reduced to a binary generalized model. It is clear that the generalized model they developed does not work for $L1_2$ type ordered structure while ours works for all the three types of ordered structure i.e. B2, $L1_0$ and $L1_2$ of binary atoms.

Next we simplify the above equation and get

$$\begin{aligned} H = {} & NZ\left\{y_A h_{AA} + \left[\left(\frac{m}{m+n}\right) - y_A - \chi - y_B\left(\frac{m}{n}\right) + \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right]h_{AB} + z_\beta h_{A\square} + \right. \\ & \left. + z_\alpha h_{B\square} + y_B h_{BB}\right\} + NZ'\left\{\left[\left(\frac{m}{m+n}\right) - 2(\chi + y_A) - z\left(\frac{m}{m+n}\right)\right]h'_{AA} + [y_B + y_A]h'_{AB} + \right. \\ & \left. + z_\alpha h'_{A\square} + z_\beta h'_{B\square} + \left[\left(\frac{n}{m+n}\right) - 2(y_B - \chi) - z\left(\frac{n}{m+n}\right)\right]h'_{BB}\right\}. \end{aligned} \quad (2.9)$$

To write the expression for the Gibbs free energy the entropy is needed in addition to the enthalpy. The entropy consists of the configurational entropy S^c in which the random distribution of each species on the two sublattices is assumed and the vibrational (phononical) entropy S^v so that the total entropy S is the sum of the two:

$$S = S^c + S^v. \tag{2.10}$$

The configurational entropy, S^c, is a function of the numbers of atoms and vacancies on the α and β sublattices given by

$$S^c = k_B \ln\left(\frac{N^\alpha!}{N_A^\alpha! N_B^\alpha! N_\square^\alpha!} \frac{N^\beta!}{N_A^\beta! N_B^\beta! N_\square^\beta!}\right). \tag{2.11}$$

Applying Stirling's approximation ($\ln \mathrm{X}! = \mathrm{X} \ln \mathrm{X}! - \mathrm{X}$) and using the relation given in Table 2.1 the above equation turns out to be

$$S^c = R\left\{\left(\frac{m}{m+n}\right)\left[z + (\chi + y_A)\left(\frac{m+n}{m}\right)\right]\ln\left(\frac{m}{m+n}\right) + \left(\frac{n}{m+n}\right)\left[z + (y_B - \chi)\left(\frac{m+n}{n}\right)\right]\ln\left(\frac{n}{m+n}\right) + \right.$$
$$+ (1 + z)\ln(1 + z) - \left[y_A \ln y_A + y_B \ln y_B + z_\alpha \ln z_\alpha + z_\beta \ln z_\beta\right] - \left(\frac{m}{m+n}\right)\left[1 + \right.$$
$$- (\chi + y_A)\left(\frac{m+n}{m}\right)\left]\ln\left[1 - (\chi + y_A)\left(\frac{m+n}{m}\right)\right] - \left(\frac{n}{m+n}\right)\left[1 - (y_B - \chi)\left(\frac{m+n}{n}\right)\right]\ln\left[1 + \right.$$
$$\left.\left. - (y_B - \chi)\left(\frac{m+n}{n}\right)\right]\right\}. \tag{2.12}$$

Here $R = Nk_B$, with k_B is Boltzmann's constant. In the same manner to the enthalpy (see above), the total vibrational entropy can be written as

$$S^v = \sum_{ij} n_{ij} S_{ij} + \sum_{ij} n'_{ij} S'_{ij}. \tag{2.13}$$

As in the expression for the enthalpy there are parameters for the entropy of the nearest- and next-nearest-neighbour interaction denoted by S_{ij} and S'_{ij}, respectively. Using these parameters an expression for S^v can be written in a similary way as that of Eq. (2.8). In fact the formulation of the vibrational entropy in a manner specified above as a linear function of the number of pairs found in the crystal structure lacks a strong physical foundation. But, from the previous studies which use these statistical thermodynamic approach, it is found that the

individual parameters S_{ij} and S'_{ij} are not dealt with, but rather certain combinations of them have a well-defined physical meaning [2]. Here again let AA, BB, AB, B□, A□ and □□ bonds have vibrational bond entropies s_{AA}, s_{BB}, s_{AB}, $s_{\mathrm{B}\square}$, $s_{\mathrm{A}\square}$ and $s_{\square\square}$, respectively, for nearest-neighbour atoms interaction and s'_{AA}, s'_{BB}, s'_{AB}, $s'_{B\square}$, $s'_{A\square}$ and $s'_{\square\square}$ for next-nearest-neighbour atoms interaction. We are then, able to express the vibrational entropy S^v in terms of defect concentrations as

$$S^v = n_{AA}s_{AA} + n_{BB}s_{BB} + n_{AB}s_{\mathrm{AB}} + n_{B\square}s_{\mathrm{B}\square} + n_{A\square}s_{\mathrm{A}\square} + n_{\square\square}s_{\square\square} + n'_{AA}s'_{AA} + n'_{BB}s'_{BB} + n'_{AB}s'_{AB} + n'_{B\square}s'_{B\square} + n'_{A\square}s'_{A\square} + n'_{\square\square}s'_{\square\square}. \quad (2.14)$$

By considering the coordination number Z for nearest-neighbour pairs and Z' for next-nearest-neighbour pairs, the expression for the vibrational entropy S^v simplifies to

$$S^v = NZ\left\{y_A s_{AA} + \left[\left(\frac{m}{m+n}\right) - y_A - \chi - y_B\left(\frac{m}{n}\right) + \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right]s_{AB} + z_\beta s_{A\square} + z_\alpha s_{B\square} + y_B s_{BB}\right\} + NZ'\left\{\left[\left(\frac{m}{m+n}\right) - 2(\chi + y_A) - z\left(\frac{m}{m+n}\right)\right]s'_{AA} + [y_B + y_A]s'_{AB} + z_\propto s'_{A\square} + z_\beta s'_{B\square} + \left[\left(\frac{n}{m+n}\right) - 2(y_B - \chi) - z\left(\frac{n}{m+n}\right)\right]s'_{BB}\right\} \quad (2.15)$$

Notice that in the same manner as the above generalized enthalpy our generalized vibrational entropy is more general than that of J. Breuer *et al*. [16]. In their work even though it was for ternary atoms, the vibrational entropy was generalized for two ordered crystals only i.e. B2 and $L1_0$. On the other hand if we see the generalized vibrational entropy for binary atoms by reducing their work, it again works only for B2 and $L1_0$ structures. Contrary to that our generalized form of vibrational entropy works for all the three binary ordered structures i.e. B2, $L1_2$ and $L1_0$. Therefore, if one wants to have a generalized Bragg-Williams model for B2, L10 and L12 structure of ternary atoms then the generalized vibrational entropy should be developed in the same manner presented in this work.

Substituting Eq. (2.12) and Eq. (2.15) into Eq. (2.10) and carrying out further simplification the expression for the total entropy, *S*, of the system is

$$S = R\left\{\left[z\left(\frac{m}{m+n}\right) + (\chi + y_A)\right]\ln\left(\frac{m}{m+n}\right) + \left[z\left(\frac{n}{m+n}\right) + (y_B - \chi)\right]\ln\left(\frac{n}{m+n}\right) + \right.$$
$$+ (1 + z)\ln(1 + z) - \left[y_A \ln y_A + y_B \ln y_B + z_\propto \ln z_\propto + z_\beta \ln z_\beta\right] - \left[\left(\frac{m}{m+n}\right) +$$
$$- (\chi + y_A)\left]\ln\left[1 - (\chi + y_A)\left(\frac{m+n}{m}\right)\right] - \left[\left(\frac{n}{m+n}\right) - (y_B - \chi)\right]\ln\left[1 - (y_B - \chi)\left(\frac{m+n}{n}\right)\right]\right\} +$$
$$+ NZ\left\{y_A s_{AA} + \left[\left(\frac{m}{m+n}\right) - y_A - \chi - y_B\left(\frac{m}{n}\right) + \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right] s_{AB} + z_\beta s_{A\square} + z_\alpha s_{B\square} + \right.$$
$$\left. + y_B s_{BB}\right\} + NZ'\left\{\left[\left(\frac{m}{m+n}\right) - 2(\chi + y_A) - z\left(\frac{m}{m+n}\right)\right] s'_{AA} + [y_B + y_A] s'_{AB} + z_\propto s'_{A\square} + \right.$$
$$\left. + z_\beta s'_{B\square} + \left[\left(\frac{n}{m+n}\right) - 2(y_B - \chi) - z\left(\frac{n}{m+n}\right)\right] s'_{BB}\right\} \qquad (2.16)$$

After substituting the above derived expressions for *H* (Eq. (2.9)) and for *S* (Eq. (2.16)) in the Gibbs free energy relationship given in Eq. (2.1), one can obtain the Gibbs free energy to be

$$G = NZ\left\{y_A h_{AA} + \left[\left(\frac{m}{m+n}\right) - y_A - \chi - y_B\left(\frac{m}{n}\right) + \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right] h_{AB} + z_\beta h_{A\square} + \right.$$
$$\left. + z_\alpha h_{B\square} + y_B h_{BB}\right\} + NZ'\left\{\left[\left(\frac{m}{m+n}\right) - 2(\chi + y_A) - z\left(\frac{m}{m+n}\right)\right] h'_{AA} + [y_B + y_A] h'_{AB} + \right.$$
$$\left. + z_\propto h'_{A\square} + z_\beta h'_{B\square} + \left[\left(\frac{n}{m+n}\right) - 2(y_B - \chi) - z\left(\frac{n}{m+n}\right)\right] h'_{BB}\right\} - RT\left\{\left[z\left(\frac{m}{m+n}\right) + \right.\right.$$
$$\left.\left. + (\chi + y_A)\right]\ln\left(\frac{m}{m+n}\right) + \left[z\left(\frac{n}{m+n}\right) + (y_B - \chi)\right]\ln\left(\frac{n}{m+n}\right) + (1 + z)\ln(1 + z) + \right.$$
$$- \left[y_A \ln y_A + y_B \ln y_B + z_\propto \ln z_\propto + z_\beta \ln z_\beta\right] - \left[\left(\frac{m}{m+n}\right) - (\chi + y_A)\right]\ln\left[1 - (\chi + \right.$$
$$\left.\left. + y_A)\left(\frac{m+n}{m}\right)\right] - \left[\left(\frac{n}{m+n}\right) - (y_B - \chi)\right]\ln\left[1 - (y_B - \chi)\left(\frac{m+n}{n}\right)\right]\right\} - NZT\left\{y_A s_{AA} + \right.$$
$$\left. + \left[\left(\frac{m}{m+n}\right) - y_A - \chi - y_B\left(\frac{m}{n}\right) + \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right] s_{AB} + z_\beta s_{A\square} + z_\alpha s_{B\square} + y_B s_{BB}\right\} +$$
$$- NZ'T\left\{\left[\left(\frac{m}{m+n}\right) - 2(\chi + y_A) - z\left(\frac{m}{m+n}\right)\right] s'_{AA} + [y_B + y_A] s'_{AB} + z_\propto s'_{A\square} + z_\beta s'_{B\square} + \right.$$
$$\left. + \left[\left(\frac{n}{m+n}\right) - 2(y_B - \chi) - z\left(\frac{n}{m+n}\right)\right] s'_{BB}\right\} \qquad (2.17)$$

The generalized Gibbs free energy *G* presented above can't be reproduced from J. Breuer *et al*. [16]. But from this *G* we can generate the generalized *G* for binary atoms derived from [16] i.e. for B2 and $L1_0$. In addition to that our *G* can give the form of Gibbs free energy for $L1_2$ structure.

2.1.2.2 Thermodynamic equilibrium

Thermodynamic equilibrium at constant temperature and pressure requires the Gibbs free energy *G* to be minimum. This implies that $(\partial G/\partial x = 0)$ and $(\partial^2 G/\partial x^2 > 0)$ at the same time where x stands for z, y_A and y_B. Thus the equilibrium defect concentrations at a specific temperature, pressure and overall composition can be obtained by minimizing *G* with respect to the three independent defect concentrations z, y_{A} and y_{B}. And applying the minimization conditions in the Gibbs free energy relationship given in Eq.(2.17) $(\partial G/\partial z = 0,\ \partial G/\partial y_A = 0$ and $\partial G/\partial y_B = 0)$ one obtains:

The minimization with respect to vacancy concentration z (i.e. $\frac{\partial G}{\partial z}\Big|_{T,p,\chi} = 0$) gives:

$$NZ\left[h_{A\square} + h_{B\square} - \left(\frac{m}{m+n}\right)h_{AB}\right] + NZ'\left[h'_{A\square} + h'_{B\square} - \left(\frac{m}{m+n}\right)h'_{AA} - \left(\frac{n}{m+n}\right)h'_{BB}\right] +$$
$$- NZT\left[S_{A\square} + S_{B\square} - S_{AB}\left(\frac{m}{m+n}\right)\right] - NZ'T\left[S'_{A\square} + S'_{B\square} - \left(\frac{m}{m+n}\right)S'_{AA} - \left(\frac{n}{m+n}\right)S'_{BB}\right] =$$
$$RT\left[\left(\frac{m}{m+n}\right)\ln\left(\frac{m}{m+n}\right) + \left(\frac{n}{m+n}\right)\ln\left(\frac{n}{m+n}\right) + \ln(1+z) - \left(\frac{m}{m+n}\right)\ln\left(\frac{mz}{m+n} + \chi + y_A +\right.\right.$$
$$\left.\left. - y_B\right) - \left(\frac{n}{m+n}\right)\ln\left(\frac{nz}{m+n} - \chi - y_A + y_B\right)\right]. \qquad (2.18a)$$

Next, the minimization with respect to the concentrations of antistructure atoms on β sublattice y_A (i.e. $\frac{\partial G}{\partial y_A}\Big|_{T,p,\chi} = 0$) gives the relation,

$$NZ[h_{AA} - h_{AB} - h_{A\square} + h_{B\square}] + NZ'[h'_{AB} + h'_{A\square} - 2h'_{AA} - h'_{B\square}] - NZT[S_{AA} + S_{AB} +$$
$$- S_{A\square} + S_{B\square}] - NZ'T[S'_{AB} + S'_{A\square} - 2S'_{AA} - S'_{B\square}] = RT\left[\ln\left(\frac{m}{m+n}\right) - \ln y_A - \ln\left(\frac{mz}{m+n} +\right.\right.$$
$$\left.\left. + \chi + y_A - y_B\right) + \ln\left(\frac{nz}{m+n} - \chi - y_A + y_B\right) + \ln\left(1 - \frac{(\chi + y_A)(m+n)}{m}\right)\right]. \quad (2.18b)$$

Lastly, applying minimization with respect to the concentration of antistructure atoms on α sublattice y_B (i.e. $\frac{\partial G}{\partial y_B}\Big|_{T,p,\chi} = 0$) we get

$$NZ\left[h_{A\square} - h_{B\square} - \left(\frac{m}{n}\right)h_{AB} + h_{BB}\right] + \frac{1}{2}NZ'[h'_{AB} - h'_{A\square} + h'_{B\square} - 2h'_{BB}] - NZT\left[S_{A\square} + \right.$$
$$\left. - S_{B\square} - \left(\frac{m}{n}\right)S_{AB} + S_{BB}\right] - NZ'T[S'_{AB} - S'_{A\square} + S'_{B\square} - 2S'_{BB}] = RT\left[\ln\left(\frac{n}{m+n}\right) + \right.$$
$$\left. - \ln y_B + \ln\left(\frac{mz}{m+n} + \chi + y_A - y_B\right) - \ln\left(\frac{nz}{m+n} - \chi - y_A + y_B\right) + \ln\left(1 + \right.\right.$$
$$\left.\left. - \frac{(y_B - \chi)(m+n)}{n}\right)\right]. \qquad (2.18c)$$

Eqs. (2.18a), (2.18b) and (2.18c) are the relations which cannot be derived from J.Breuer *et al*. [16] or any previous generalized Bragg-Williams model. The equations express the relationship between the equilibrium defect concentrations of a given amount of concentration of atoms at a certain temperature with a known value of interaction enthalpies and entropies of nearest- and next-nearest-neighbour atoms. These equations, different from other generalized equations, can be used for any of the three ordered structures (i.e. B2, $L1_0$ and $L1_2$) of a binary intermetallic compounds by fixing the appropriate values of the parameters of m, n and Z.

2.1.3 Thermodynamic activities

Activity is potential for chemical reaction. It is the ability of a substance to undergo a chemical reaction. It is known that activity data for components A and B of the binary intermetallic compounds can be determined experimentally. In the following, we derive equations that enable us to evaluate the thermodynamic activities of components A and B.

The value of the Gibbs free energy for component i ($i = A$ or B), G_i, is related to the thermodynamic activity, a_i, by

$$G_i = G_i^0 + RT \ln a_i. \qquad (2.19)$$

In particular,

$$\ln a_{\mathrm{A}} = \frac{1}{RT}G_A - \frac{1}{RT}G_A^0, \qquad (2.20a)$$

and

$$\ln a_B = \frac{1}{RT}G_{\mathrm{B}} - \frac{1}{RT}G_B^0. \qquad (2.20b)$$

where G_A^0 and G_B^0 are the partial Gibbs free energy for components A and B, respectively, in a standard state. On the other hand, the partial Gibbs free energy for components A and B, which is G_A and G_B, respectively , in a binary system is derived from the Gibbs free energy, G, as

$$G_A = G + \left(1 - \frac{N_A}{N}\right) N \frac{\partial G}{\partial N_A} - \frac{N_B}{N} N \frac{\partial G}{\partial N_B}, \tag{2.21a}$$

$$G_B = G - \frac{N_A}{N} N \frac{\partial G}{\partial N_A} + \left(1 - \frac{N_B}{N}\right) N \frac{\partial G}{\partial N_B}. \tag{2.21b}$$

In the above equations there are two variables N_A and N_B. We now replace the parameters of N_A and N_B by the concentration variable χ. The relation $\left(\frac{\partial G}{\partial N_{A(B)}}\right)$ appropriately indicates functional relation between G and $N_{A(B)}$. Note that

$$\left(\frac{\partial G}{\partial N_A}\right) = \left(\frac{\partial G}{\partial \chi}\right)\left(\frac{\partial \chi}{\partial N_A}\right) = -\frac{1}{N}\left(\frac{\partial G}{\partial \chi}\right), \tag{2.22a}$$

and

$$\left(\frac{\partial G}{\partial N_B}\right) = \left(\frac{\partial G}{\partial \chi}\right)\left(\frac{\partial \chi}{\partial N_B}\right) = \frac{1}{N}\left(\frac{\partial G}{\partial \chi}\right). \tag{2.22b}$$

By substituting Eqs. (2.22a), (2.22b) and using assumption 4 in Eqs. (2.21a) and (2.21b), the Gibbs free energy for each component G_A and G_B takes the form

$$G_A = G - 2\left(\chi + \frac{n}{m+n}\right)\frac{\partial G}{\partial \chi}, \tag{2.23a}$$

and

$$G_B = G + 2\left(\frac{m}{m+n} - \chi\right)\frac{\partial G}{\partial \chi}, \tag{2.23b}$$

respectively. Inserting the above derived expression for G (Eq. (2.17)) into (Eq. (2.23a) and Eq. (2.23b)), we get the following expressions for G_{A} and G_{B}:

$$G_A = NZ\left\{y_A h_{AA} + \left[\left(\frac{2n-m}{m+n}\right) - y_A + \chi - y_B\left(\frac{m}{n}\right) - \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right] h_{AB} + \left[\left(\frac{2n}{m+n}\right) + \right.\right.$$
$$+ \chi - y_A + y_B + \left(\frac{n}{m+n}\right) z\Big] h_{A\square} - \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B - \left(\frac{m}{m+n}\right) z\right] h_{B\square} + y_B h_{BB}\Big\} +$$
$$+ NZ'\left\{\left[\left(\frac{4n+m}{m+n}\right) + 2\chi - 2y_A - z\left(\frac{m}{m+n}\right)\right] h'_{AA} + [y_B + y_A] h'_{AB} - \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + \right.\right.$$
$$+ y_B - \left(\frac{m}{m+n}\right) z\Big] h'_{A\square} + \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B + \left(\frac{n}{m+n}\right) z\right] h'_{B\square} - \left[\left(\frac{3n}{m+n}\right) + 2\chi + 2y_B + \right.$$
$$+ z\left(\frac{n}{m+n}\right)\Big] h'_{BB}\Big\} + RT\left\{\left(2\chi + \frac{2n}{m+n}\right)\ln\left(\tfrac{m}{n}\right) - \left[z\left(\frac{m}{m+n}\right) + (\chi + y_A)\right]\ln\left(\frac{m}{m+n}\right) + \right.$$
$$- \left[z\left(\frac{n}{m+n}\right) + (y_B - \chi)\right]\ln\left(\frac{n}{m+n}\right) - (1+z)\ln(1+z) + y_A \ln y_A + y_B \ln y_B +$$
$$+ \left[\left(\frac{m}{m+n}\right) z - \chi + y_A - y_B - \left(\frac{2n}{m+n}\right)\right]\ln\left[\left(\frac{m}{m+n}\right) z + \chi + y_A - y_B\right] + \left[\left(\frac{n}{m+n}\right) z + \chi + \right.$$
$$- y_A + y_B + \left(\frac{2n}{m+n}\right)\Big]\ln\left[\left(\frac{n}{m+n}\right) z - \chi - y_A + y_B\right] + \left[\left(\frac{2n+m}{m+n}\right) + \chi - y_A\right]\ln\left[1 - (\chi + \right.$$
$$+ y_A)\left(\frac{m+n}{m}\right)\Big] - \left[\left(\frac{n}{m+n}\right) + \chi + y_B\right]\ln\left[1 - (y_B - \chi)\left(\frac{m+n}{n}\right)\right]\Big\} - NZT\left\{y_A s_{AA} + \right.$$
$$+ \left[\left(\frac{2n-m}{m+n}\right) - y_A + \chi - y_B\left(\frac{m}{n}\right) - \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right] s_{AB} + \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B + \right.$$
$$+ \left(\frac{n}{m+n}\right) z\Big] s_{A\square} - \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B - \left(\frac{m}{m+n}\right) z\right] s_{B\square} + y_B s_{BB}\Big\} - NZ'T\left\{\left[\left(\frac{4n+m}{m+n}\right) + \right.\right.$$
$$+ 2\chi - 2y_A - z\left(\frac{m}{m+n}\right)\Big] s'_{AA} + [y_B + y_A] s'_{AB} - \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B - \left(\frac{m}{m+n}\right) z\right] s'_{A\square} + \left.\right.$$
$$+ \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B + \left(\frac{n}{m+n}\right) z\right] s'_{B\square} - \left[\left(\frac{3n}{m+n}\right) + 2\chi + 2y_B + z\left(\frac{n}{m+n}\right)\right] s'_{BB}\Big\} \quad (2.24a)$$

and,

$$G_B = NZ\left\{y_A h_{AA} + \left[\left(\frac{2m}{m+n}\right)\left(\frac{m}{n}\right) - \left(\frac{m}{m+n}\right) - \chi\left(\frac{m}{n}\right) + \chi - y_A - y_B\left(\frac{m}{n}\right) + \right.\right.$$
$$- z\left(\frac{m}{m+n}\right)\Big] h_{AB} - \left[\left(\frac{2m}{m+n}\right) - \chi + y_A - y_B - z\left(\frac{n}{m+n}\right)\right] h_{A\square} + \left[\left(\frac{2m}{m+n}\right) - \chi + y_A + \right.$$
$$- y_B + z\left(\frac{m}{m+n}\right)\Big] h_{B\square} + y_B h_{BB}\Big\} + NZ'\left\{\left[\left(\frac{-3m}{m+n}\right) + 2\chi - 2y_A - z\left(\frac{m}{m+n}\right)\right] h'_{AA} + \right.$$
$$+ [y_B + y_A] h'_{AB} - \left[\left(\frac{2m}{m+n}\right) - \chi + y_A - y_B + z\left(\frac{m}{m+n}\right)\right] h'_{A\square} - \left[\left(\frac{2m}{m+n}\right) - \chi + y_A + \right.$$
$$- y_B - z\left(\frac{n}{m+n}\right)\Big] h'_{B\square} + \left[\left(\frac{4m+n}{m+n}\right) - 2\chi - 2y_B - z\left(\frac{n}{m+n}\right)\right] h'_{BB}\Big\} - RT\left\{\left(\frac{2m}{m+n} + \right.\right.$$
$$- 2\chi\Big)\ln\left(\tfrac{m}{n}\right) + \left[z\left(\frac{m}{m+n}\right) + (\chi + y_A)\right]\ln\left(\frac{m}{m+n}\right) + \left[z\left(\frac{n}{m+n}\right) + (y_B - \chi)\right]\ln\left(\frac{n}{m+n}\right) +$$
$$+ (1+z)\ln(1+z) - y_A \ln y_A - y_B \ln y_B +$$
$$- \left[\left(\frac{2m}{m+n}\right) - \chi + y_A - y_B + z\left(\frac{m}{m+n}\right)\right]\ln\left[\left(\frac{m}{m+n}\right) z + \chi + y_A - y_B\right] + \left[\left(\frac{2m}{m+n}\right) - \chi + \right.$$
$$+ y_A - y_B - z\left(\frac{n}{m+n}\right)\Big]\ln\left[\left(\frac{n}{m+n}\right) z - \chi - y_A + y_B\right] + \left(\frac{m}{m+n} - \chi + y_A\right)\ln\left[1 - (\chi + \right.$$
$$+ y_A)\left(\frac{m+n}{m}\right)\Big] - \left[\left(\frac{2m+n}{m+n}\right) - \chi - y_B\right]\ln\left[1 - (y_B - \chi)\left(\frac{m+n}{n}\right)\right]\Big\} - NZT\left\{y_A s_{AA} + \right.$$
$$+ \left[\left(\frac{2n-m}{m+n}\right) - y_A + \chi - y_B\left(\frac{m}{n}\right) - \chi\left(\frac{m}{n}\right) - z\left(\frac{m}{m+n}\right)\right] s_{AB} + \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B + \right.$$
$$+ \left(\frac{n}{m+n}\right) z\Big] s_{A\square} - \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B - \left(\frac{m}{m+n}\right) z\right] s_{B\square} + y_B s_{BB}\Big\} +$$
$$- NZ'T\left\{\left[\left(\frac{4n+m}{m+n}\right) + 4\chi - 2y_A - z\left(\frac{m}{m+n}\right)\right] s'_{AA} + [y_B + y_A] s'_{AB} - \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + \right.\right.$$
$$+ y_B - \left(\frac{m}{m+n}\right) z\Big] s'_{A\square} + \left[\left(\frac{2n}{m+n}\right) + \chi - y_A + y_B + \left(\frac{n}{m+n}\right) z\right] s'_{B\square} - \left[\left(\frac{3n}{m+n}\right) + 2\chi + 2y_B + \right.$$
$$+ z\left(\frac{n}{m+n}\right)\Big] s'_{BB}\Big\} \quad (2.24b)$$

At last, the equation for the thermodynamic activity of components A and B can be derived as follows. Inserting Eqs. (2.24a) and (2.24b) into Eqs. (2.20a) and (2.20b), respectively, gives the final generalized thermodynamic activity equation for each component atom of the ordered binary intermetallic compounds.

$$\ln a_{\mathrm{A}} = \frac{Z}{kT}\Big\{y_A h_{AA} + \Big[\Big(\frac{2n-m}{m+n}\Big) - y_A + \chi - y_B\Big(\frac{m}{n}\Big) - \chi\Big(\frac{m}{n}\Big) - z\Big(\frac{m}{m+n}\Big)\Big]h_{AB} + \Big[\Big(\frac{2n}{m+n}\Big) + \\ + \chi - y_{\mathrm{A}} + y_{\mathrm{B}} + \Big(\frac{n}{m+n}\Big)z\Big]h_{A\square} - \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_{\mathrm{A}} + y_{\mathrm{B}} - \Big(\frac{m}{m+n}\Big)z\Big]h_{B\square} + y_B h_{BB}\Big\} + \\ + \frac{Z'}{kT}\Big\{\Big[\Big(\frac{4n+m}{m+n}\Big) + 2\chi - 2y_A - z\Big(\frac{m}{m+n}\Big)\Big]h'_{AA} + [y_B + y_A]h'_{AB} - \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_{\mathrm{A}} + \\ + y_{\mathrm{B}} - \Big(\frac{m}{m+n}\Big)z\Big]h'_{A\square} + \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_{\mathrm{A}} + y_{\mathrm{B}} + \Big(\frac{n}{m+n}\Big)z\Big]h'_{B\square} - \Big[\Big(\frac{3n}{m+n}\Big) + 2\chi + 2y_B + \\ + z\Big(\frac{n}{m+n}\Big)\Big]h'_{BB}\Big\} + \Big\{\Big(2\chi + \frac{2n}{m+n}\Big)\ln\Big(\frac{m}{n}\Big) - \Big[z\Big(\frac{m}{m+n}\Big) + (\chi + y_A)\Big]\ln\Big(\frac{m}{m+n}\Big) + \\ - \Big[z\Big(\frac{n}{m+n}\Big) + (y_B - \chi)\Big]\ln\Big(\frac{n}{m+n}\Big) - (1+z)\ln(1+z) + y_A \ln y_A + y_B \ln y_B + \\ + \Big[\Big(\frac{m}{m+n}\Big)z - \chi + y_{\mathrm{A}} - y_{\mathrm{B}} - \Big(\frac{2n}{m+n}\Big)\Big]\ln\Big[\Big(\frac{m}{m+n}\Big)z + \chi + y_{\mathrm{A}} - y_{\mathrm{B}}\Big] + \Big[\Big(\frac{n}{m+n}\Big)z + \chi + \\ - y_{\mathrm{A}} + y_{\mathrm{B}} + \Big(\frac{2n}{m+n}\Big)\Big]\ln\Big[\Big(\frac{n}{m+n}\Big)z - \chi - y_{\mathrm{A}} + y_{\mathrm{B}}\Big] + \Big[\Big(\frac{2n+m}{m+n}\Big) + \chi - y_A\Big]\ln\Big[1 - (\chi + \\ + y_A)\Big(\frac{m+n}{m}\Big)\Big] - \Big[\Big(\frac{n}{m+n}\Big) + \chi + y_B\Big]\ln\Big[1 - (y_B - \chi)\Big(\frac{m+n}{n}\Big)\Big]\Big\} - \frac{Z}{k}\Big\{y_A s_{AA} + \\ + \Big[\Big(\frac{2n-m}{m+n}\Big) - y_A + \chi - y_B\Big(\frac{m}{n}\Big) - \chi\Big(\frac{m}{n}\Big) - z\Big(\frac{m}{m+n}\Big)\Big]s_{AB} + \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_{\mathrm{A}} + y_{\mathrm{B}} + \\ + \Big(\frac{n}{m+n}\Big)z\Big]s_{A\square} - \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_{\mathrm{A}} + y_{\mathrm{B}} - \Big(\frac{m}{m+n}\Big)z\Big]s_{B\square} + y_B s_{BB}\Big\} - \frac{Z'}{k}\Big\{\Big[\Big(\frac{4n+m}{m+n}\Big) + \\ + 2\chi - 2y_A - z\Big(\frac{m}{m+n}\Big)\Big]s'_{AA} + [y_B + y_A]s'_{AB} - \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_{\mathrm{A}} + y_{\mathrm{B}} - \Big(\frac{m}{m+n}\Big)z\Big]s'_{A\square} + \\ + \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_{\mathrm{A}} + y_{\mathrm{B}} + \Big(\frac{n}{m+n}\Big)z\Big]s'_{B\square} - \Big[\Big(\frac{3n}{m+n}\Big) + 2\chi + 2y_B + z\Big(\frac{n}{m+n}\Big)\Big]s'_{BB}\Big\} - \frac{1}{RT}G_A^0 \tag{2.25a}$$

and,

$$\ln a_B = \frac{Z}{kT}\Big\{y_A h_{AA} + \Big[\Big(\frac{2m}{m+n}\Big)\Big(\frac{m}{n}\Big) - \Big(\frac{m}{m+n}\Big) - \chi\Big(\frac{m}{n}\Big) + \chi - y_A - y_B\Big(\frac{m}{n}\Big) +$$
$$- z\Big(\frac{m}{m+n}\Big)\Big] h_{AB} - \Big[\Big(\frac{2m}{m+n}\Big) - \chi + y_A - y_B - z\Big(\frac{n}{m+n}\Big)\Big] h_{A\square} + \Big[\Big(\frac{2m}{m+n}\Big) - \chi + y_A +$$
$$- y_B + z\Big(\frac{m}{m+n}\Big)\Big] h_{B\square} + y_B h_{BB}\Big\} + \frac{Z'}{kT}\Big\{\Big[\Big(\frac{-3m}{m+n}\Big) + 2\chi - 2y_A - z\Big(\frac{m}{m+n}\Big)\Big] h'_{AA} +$$
$$+ [y_B + y_A] h'_{AB} - \Big[\Big(\frac{2m}{m+n}\Big) - \chi + y_A - y_B + z\Big(\frac{m}{m+n}\Big)\Big] h'_{A\square} - \Big[\Big(\frac{2m}{m+n}\Big) - \chi + y_A +$$
$$- y_B - z\Big(\frac{n}{m+n}\Big)\Big] h'_{B\square} + \Big[\Big(\frac{4m+n}{m+n}\Big) - 2\chi - 2y_B - z\Big(\frac{n}{m+n}\Big)\Big] h'_{BB}\Big\} - \Big\{\Big(\frac{2m}{m+n} - 2\chi\Big)\ln\Big(\frac{m}{n}\Big) +$$
$$+ \Big[z\Big(\frac{m}{m+n}\Big) + (\chi + y_A)\Big]\ln\Big(\frac{m}{m+n}\Big) + \Big[z\Big(\frac{n}{m+n}\Big) + (y_B - \chi)\Big]\ln\Big(\frac{n}{m+n}\Big) + (1 +$$
$$+ z)\ln(1 + z) - y_A \ln y_A - y_B \ln y_B +$$
$$- \Big[\Big(\frac{2m}{m+n}\Big) - \chi + y_A - y_B + z\Big(\frac{m}{m+n}\Big)\Big]\ln\Big[\Big(\frac{m}{m+n}\Big) z + \chi + y_A - y_B\Big] + \Big[\Big(\frac{2m}{m+n}\Big) - \chi +$$
$$+ y_A - y_B - \boldsymbol{z}\Big(\frac{n}{m+n}\Big)\Big]\ln\Big[\Big(\frac{n}{m+n}\Big) z - \chi - y_A + y_B\Big] + \Big(\frac{m}{m+n} - \chi + y_A\Big)\ln\Big[1 - (\chi +$$
$$+ y_A)\Big(\frac{m+n}{m}\Big)\Big] - \Big[\Big(\frac{2m+n}{m+n}\Big) - \chi - y_B\Big]\ln\Big[1 - (y_B - \chi)\Big(\frac{m+n}{n}\Big)\Big]\Big\} - \frac{Z}{k}\Big\{y_A s_{AA} +$$
$$+ \Big[\Big(\frac{2n-m}{m+n}\Big) - y_A + \chi - y_B\Big(\frac{m}{n}\Big) - \chi\Big(\frac{m}{n}\Big) - z\Big(\frac{m}{m+n}\Big)\Big] s_{AB} + \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_A + y_B +$$
$$+ \Big(\frac{n}{m+n}\Big) z\Big] s_{A\square} - \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_A + y_B - \Big(\frac{m}{m+n}\Big) z\Big] s_{B\square} + y_B s_{BB}\Big\} - \frac{Z'}{k}\Big\{\Big[\Big(\frac{4n+m}{m+n}\Big) +$$
$$+ 4\chi - 2y_A - z\Big(\frac{m}{m+n}\Big)\Big] s'_{AA} + [y_B + y_A] s'_{AB} - \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_A + y_B +$$
$$- \Big(\frac{m}{m+n}\Big) z\Big] s'_{A\square} + \Big[\Big(\frac{2n}{m+n}\Big) + \chi - y_A + y_B + \Big(\frac{n}{m+n}\Big) z\Big] s'_{B\square} - \Big[\Big(\frac{3n}{m+n}\Big) + 2\chi + 2y_B +$$
$$+ z\Big(\frac{n}{m+n}\Big)\Big] s'_{BB}\Big\} - \frac{1}{RT} G_B^0. \qquad (2.25b)$$

2.1.4 The relationship between *H* and Δ*H*

The following equation shows the relation between the total enthalpy (*H*) and the enthalpy of formation (Δ*H*). Δ*H* can be experimentally determined (e.g. by solution calorimetry). The experimentally accessible enthalpy of formation Δ*H* is given by

$$\Delta H = H - \Big[\frac{N_A}{N} H_A + \frac{N_B}{N} H_B\Big]. \qquad (2.26)$$

We can rewrite the above equation as

$$\Delta H = H - \left[\left(\frac{m}{m+n} - \chi\right) H_A + \left(\chi + \frac{n}{m+n}\right) H_B\right], \qquad (2.27)$$

where H_A and H_B are the enthalpies per mole of the pure element at the same temperature and pressure as pertaining to H and ΔH.

To the best of our knowledge the generalized statistical thermodynamic model presented here is our original work which is not done by others before. The generalized statistical thermodynamic model of the Bragg-Williams approach for ternary intermetallic compounds having structure of B2 and $L1_0$ type acquiring up to *four* (hybrid) point defect was presented by J. Breuer *et al* [16]. But here a generalized statistical thermodynamic model of the Bragg-Williams approach for binary ordered intermetallic compounds having structure of B2, $L1_2$ and $L1_0$ type acquiring up to *four* (hybrid) point defects is presented. The other point is that every equation in this generalized formulation can't be regenerated from other generalized models of the Bragg-Williams type because it is more general than that of any other model of such type. If one compares this work with a pair interaction model of [16], it is not difficult to notice the existence of basic difference from the beginning. In that work it started by fixing partially the value of variables *n* and *m* from the beginning. Due to this one can say, that work was generalized for B_2 and $L1_0$ type structures only [16]. In general our work can be applied to binary ordered intermetallics having any of the three structure acquiring mono vacancy, antistructure, triple, three or *four* (hybrid) defect.

As we mentioned above, an ordered binary intermetallic compound can have a certain type of defect or another. This happens because of the presence or absence of vacancy or antistructure atom in either of the sublattices of the ordered binary intermetallics. Now, if one wants to apply the model, first he needs to modify all the necessary equations of the generalized once to the appropriate form depending on the type of structure and the defect type. For three common ordered structures constituted of two sublattices (B2, $L1_0$ and $L1_2$) the model equations for the enthalpy of formation (Eqs. (2.28), the thermodynamic activity (Eqs. (2.26a) and (2.26b)) and the three minimization conditions which govern the point defect concentrations (Eqs. (2.19a, 2.19b and 2.19c)) can be obtained easily by inserting *m*, *n*, *Z* and *Z'* data given in Table 2.2.

Table 2.2: *m* and *n* numbers and coordination numbers for nearest (Z) and next nearest neighbours (Z') of three ordered crystal structures.

Structure	Prototype	m	n	Z	Z'
B2	CsCl	1	1	8	6
$L1_0$	CuAu	1	1	12	6
$L1_2$	Cu_3Au	3	1	12	6

2.2 Applications of the Bragg-Williams method

The generalized model presented in this Chapter can be modified into different types of defect models depending on the selected types of binary ordered structure intermetallic compounds. In any of the B2, $L1_2$ or $L1_0$ ordered structured intermetallic compounds there can be mono vacancy in one kind of intermetallic compound, triple defect on another, three defect or hybrid defect again in another. According to the type of structure and defect, it is required to modify the Bragg-Williams model to determine the defect parameters.

The generalized model can be modified to work for the *four* defect model. First it is important to select the type of binary ordered structure and put the appropriate values of *Z*, *Z'*, *n* and *m*. In the case of *four* (hybrid) defect there are antistructure atoms on both sublattices and vacancy on both sublattices. Using very accurate enthalpy of formation data and activity data the model parameters h_{ij}, h'_{ij}, s_{ij} and s'_{ij} (i.e. including up to next-nearest-neighbour interactions) can be determined and the defect concentrations can be calculated.

If the experimentally determined natural logarithm of B type atom activity and the experimentally determined enthalpy of formation for a given binary ordered intermetallic compound is available, then by, *simultaneous* fitting of the enthalpy of formation data and the thermodynamic activity data, both as a function of composition, leads to very good descriptions of the experimental input data. Inserting the thereby obtained model parameters (four enthalpy parameters and four entropy parameters) into the model equations, the defect concentrations can be calculated as a function of composition. The experimentally determined defect concentration data can be fitted to the calculated defect concentration curves and then checked its full consistency.

Using the model with the obtained parameters, also calculations for temperatures other than the one pertaining to the thermodynamic input data can be performed. The thus obtained values for the effective enthalpy, $h_{\square}^{eff}(\chi)$, and entropy of formation of vacancies, $s_{\square}^{eff}(\chi)$, according to the Arrhenius relation $z(\chi,T) = \exp(s_{\square}^{eff}(\chi)/k)\exp(-h_{\square}^{eff}(\chi)/kT)$, can be checked whether it agrees very well with the results of ab initio calculations or not.

To describe the experimentally determined vacancy concentration curve as a function of composition and temperature, the model described can be applied. However, inserting the model parameters obtained by fitting to the vacancy concentration data as a function of composition at higher temperatures, the temperature dependence of the vacancy concentration as calculated by the model is unusual. It means that at absolute zero temperature no vacancies would exist and all defects would be antistructure atoms. On the other hand raising the temperature by only a few degrees, the vacancy concentration shoots up to its almost temperature independent high level.

For the calculation of the effective enthalpy and entropy of formation of vacancies in the framework of the given model one may use the following recipe: solve Eq. (2.18b) for y_B, insert into Eqs. (2.18a) and (2.18c), solve Eq. (2.18c) for y_A and insert into Eq. (2.18a), solve for z. Then, from comparison of the obtained equation with the usual Arrhenius-type relation, one can identify the effective enthalpy and entropy of the vacancy formation.

Provided with sufficient experimental data for thermodynamic properties (i.e. enthalpy of formation data and data for the thermodynamic activity), that allow reliable assessment of the interaction parameters, the statistical method based on the Bragg-Williams approach provides a powerful instrument for the determination of types and concentrations of point defects. The revisited statistical-thermodynamic method applying pair interactions is a viable approximation of nature that leads to satisfactory predictions on atomic level from knowledge of properties on macroscopic level.

CHAPTER THREE

A Bragg-Williams model for binary B2 intermetallic compounds with hybrid defect

3.1 Models for hydride defect in B2 intermetallic compounds

3.1.1 Four defect type model

In this chapter a model for a hybrid point defect formation in B2 intermetallic compounds will be formulated using the generalized model presented in Chapter two. There are models designed for the description of thermodynamic properties of B2 intermetallic compounds acquiring triple defect and three defect types by incorporating nearest-neighbour pair interaction terms only [27]. There is no previous model designed for more complex type of point defect called hybrid (*four*) defect type of B2 intermetallic compounds. In the hybrid defect type model vacancies occur on both α and β sublattices, and antistructure atoms also occur on both sublattices. The distribution of the atoms and defects on the two sublattices are given in Table 2.1 in Chapter two. In the hybrid defect type model there are three independent variables: the vacancy concentration z, the concentration of antistructure atoms on the β sublattice y_A and the concentration of antistructure atoms on the α sublattice y_B. Knowing these quantities the other defect concentration, i.e. the vacancy concentration on the α sublattice z_α and the vacancy concentration on the β sublattice z_β, can be calculated [3]. In the following section we will develop equations for calculating composition and temperature dependence of a hybrid defect. Here we will use the same approach as in [27] so that we will consider only nearest neighbour pair interactions.

3.1.2 Composition and temperature dependence of thermodynamic properties according to the four defect types model

In order to get equations that relate the dependence of composition and temperature on the hybrid defect, we first derive the expression for the enthalpy H and the entropy S of B2 type hybrid defect and substitute them into the equation for Gibbs free energy G. The condition for

equilibrium requires that we minimize G with respect to defect parameters which will enable us to determine the relationship between the defect parameters with composition and temperature. In addition, we will find the expression for the enthalpy of formation ΔH and the thermodynamic activity $a_{A(B)}$ to determine the relationship between defect parameters with composition and temperature. This relation will enable us to generate thermodynamic data using available experimental data of thermodynamic activity and enthalpy of formation by fitting.

From the generalized model developed in the previous Chapter, we can get the expression for the enthalpy H of the B2-$A_{1-x}B_x$ compound acquiring *four* defect according to the Bragg-Williams approach. In Eq. (2.9) taking m=1, n=1 and Z=8 for B2-type gives,

$$H = 4N[(1-2\chi)h_{AB} + 2\chi h_{BB}] - (z - 2\chi + 2y_A + 2y_B)\Delta H_{AB} + (z - 2\chi - 2y_{\mathrm{A}} + + 2y_{\mathrm{B}})\Delta H_{A\square} + (z + 2\chi + 2y_{\mathrm{A}} - 2y_{\mathrm{B}})\Delta H_{B\square} \quad (3.1)$$

where

$$\Delta H_{AB} = 4N\left[h_{AB} - \frac{(h_{AA} + h_{BB})}{2}\right], \quad (3.2a)$$

$$\Delta H_{A\square} = 4N\left[h_{A\square} - \frac{h_{AA}}{2}\right], \quad (3.2b)$$

and

$$\Delta H_{B\square} = 4N\left[h_{B\square} - \frac{h_{BB}}{2}\right]. \quad (3.2c)$$

The terms ΔH_{ij} have the same meaning as in [27], with Nh_{ij} as the enthalpy value per mole connected with the 'bond' ij. On the other hand, the enthalpy of formation ΔH is given by

$$\Delta H = H - \left[\left(\frac{1}{2} - \chi\right)H_A + \left(\chi + \frac{1}{2}\right)H_B\right] \quad (3.3)$$

where H_i (i=A,B) are the enthalpies per mole of the pure elements at the same temperature and pressure as pertaining to the enthalpy H. From Eq. (2.24a) and (2.24b), the values of H_A and H_B can be derived for B2 type ordered intermetallic compound. Hence,

$$\Delta H = N[(2\chi - 1)(3h_{AA} + 3h_{BB} - 4h_{AB})] - \left(\frac{3}{2} - 2\chi\right)\Delta H_{AB} \quad (3.4)$$

Analogous to the enthalpy above Eq. (3.1), the vibrational entropy (S^{vib}) for the same system is gives by

$$S^{vib} = 4N[(1-2\chi)s_{AB} + 2\chi s_{BB}] - (z - 2\chi + 2y_A + 2y_B)\Delta S_{AB} + (z - 2\chi - 2y_{\mathrm{A}} + \\ + 2y_{\mathrm{B}})\Delta S_{A\square} + (z + 2\chi + 2y_{\mathrm{A}} - 2y_{\mathrm{B}})\Delta S_{B\square} \quad (3.5)$$

where

$$\Delta S_{AB} = 4N\left[s_{AB} - \frac{(s_{AA}+s_{BB})}{2}\right], \quad (3.6a)$$

$$\Delta S_{A\square} = 4N\left[s_{A\square} - \frac{s_{AA}}{2}\right], \quad (3.6b)$$

and

$$\Delta S_{B\square} = 4N\left[s_{B\square} - \frac{s_{BB}}{2}\right]. \quad (3.6c)$$

The formulation of the vibrational entropy as a linear function of the number of pairs found in the structure (Eq. (3.5)) is lacking a strong physical foundation. In the following the total amount of the vibrational entropy is dealt with instead of the individual parameters s_{ij}. The given definition may be compared with the approach by Wagner who wrote the vibrational entropy in terms of a linear function of the number of atoms [14].

The configurational entropy (S^{conf}) for B2 can be derived by taking n=1, m=1 and Z=8 in to Eq. (2.12) so that

$$S^{conf} = \frac{R}{2}\Big[2(1+z)\ln(1+z) - 2y_A \ln y_A - 2y_B \ln y_B - 2\left(\frac{z}{2} + \chi + y_{\mathrm{A}} - y_{\mathrm{B}}\right)\ln\left(\frac{z}{2} + \chi + \\ + y_{\mathrm{A}} - y_{\mathrm{B}}\right) - 2\left(\frac{z}{2} - \chi - y_{\mathrm{A}} + y_{\mathrm{B}}\right)\ln\left(\frac{z}{2} - \chi - y_{\mathrm{A}} + y_{\mathrm{B}}\right) - (1-2\chi-2y_A)\ln(1-2\chi-2y_A) + \\ - (1+2\chi-2y_B)\ln(1+2\chi-2y_B) - 2(z+y_A+y_B)\ln 2\Big] \quad (3.7)$$

Inserting Eqs. (3.1), (3.5) and (3.7) into the expression for the Gibbs free energy $\left[G = H - T\left(S^{vib} + S^{conf}\right)\right]$ we get,

$$G = 4N[(1-2\chi)h_{AB} + 2\chi h_{BB}] - (z - 2\chi + 2y_A + 2y_B)\Delta H_{AB} + (z - 2\chi - 2y_A + \\ + 2y_B)\Delta H_{A\square} + (z + 2\chi + 2y_A - 2y_B)\Delta H_{B\square} - T\{4N[(1-2\chi)s_{AB} + 2\chi s_{BB}] + \\ -(z - 2\chi + 2y_A + 2y_B)\Delta S_{AB} + (z - 2\chi - 2y_A + 2y_B)\Delta S_{A\square} + (z + 2\chi + 2y_A + \\ -2y_B)\Delta S_{B\square} + RT\left[(1+z)\ln(1+z) - y_A \ln y_A - y_B \ln y_B - \left(\frac{z}{2} + \chi + y_A - y_B\right)\ln\left(\frac{z}{2} + \right.\right. \\ \left.\left. + \chi + y_A - y_B\right) - \left(\frac{z}{2} - \chi - y_A + y_B\right)\ln\left(\frac{z}{2} - \chi - y_A + y_B\right) - \left(\frac{1}{2} - \chi - y_A\right)\ln(1 + \\ -2\chi - 2y_A) - \left(\frac{1}{2} + \chi - y_B\right)\ln(1 + 2\chi - 2y_B) - (z + y_A + y_B)\ln 2\right]\}. \qquad (3.8)$$

At equilibrium G takes a minimum value with respect to the defect variables z, y_A and y_B. From Eq. (3.8), calculating $\partial G/\partial Z = 0$, $\partial G/\partial y_A = 0$ and $\partial G/\partial y_B = 0$ (equilibrium at constant temperature and pressure) term by term gives

$$4(\Delta H_{AB} - T\Delta S_{AB}) = RT \ln\left[\frac{(1-2\chi-2y_A)(1+2\chi-2y_B)}{16 y_A y_B}\right], \qquad (3.9a)$$

$$4(\Delta H_{A\square} - T\Delta S_{A\square}) = RT \ln\left[\frac{(1-2\chi-2y_A)(z-2\chi-2y_A+2y_B)^2}{4y_A(1+z)^2}\right], \qquad (3.9b)$$

and

$$4(\Delta H_{B\square} - T\Delta S_{B\square}) = RT \ln\left[\frac{(1+2\chi-2y_B)(z+2\chi+2y_A-2y_B)^2}{4y_B(1+z)^2}\right], \qquad (3.9c)$$

respectively.

After carrying out certain manipulation the above equation gives

$$y_B = \frac{(1+2\chi)J_A}{4(z-K)+2J_A}, \qquad (3.10)$$

$$y_A = \frac{(1-2\chi)J_B}{4(z-K)+2J_B}, \qquad (3.11)$$

and

$$2\chi + \frac{(1-2\chi)J_B}{2(z-K)+J_B} - \frac{(1+2\chi)J_A}{2(z-K)+J_A} = K, \qquad (3.12)$$

where

$$J_A = (1+z)^2 \mathrm{e}^{\frac{4(\Delta G_{A\square} - \Delta G_{AB})}{RT}},$$

$$J_B = (1+z)^2 \mathrm{e}^{\frac{4(\Delta G_{B\square} - \Delta G_{AB})}{RT}},$$

$$K = \left\{ z^2 - \mathrm{e}^{\frac{2(\Delta G_{A\square} + \Delta G_{B\square} - \Delta G_{AB})}{RT}} \right\}^{\frac{1}{2}},$$

$$\Delta G_{AB} = \Delta H_{AB} - T\Delta S_{AB},$$

$$\Delta G_{A\square} = \Delta H_{A\square} - T\Delta S_{A\square},$$

and $\Delta G_{B\square} = \Delta H_{B\square} - T\Delta S_{B\square}$.

Eq. (3.12) states that for known parameters of ΔH_{AB}, $\Delta H_{A\square}$, $\Delta H_{B\square}$, ΔS_{AB}, $\Delta S_{B\square}$ and $\Delta S_{A\square}$ the vacancy concentration z is an implicit function of the temperature T and the composition variable χ. Similarly, Eqs. (3.10) and (3.11) are implicit functions of composition variable χ, the vacancy concentration z and the temperature T for known parameters of ΔH_{AB}, $\Delta H_{A\square}$, $\Delta H_{B\square}$, ΔS_{AB}, $\Delta S_{B\square}$ and $\Delta S_{A\square}$ of the concentration of antistructure atoms on the β sublattice y_A and the concentration of antistructure atoms on the α sublattice y_B, respectively.

From Eqs. (2.23a) and (2.23b) the dependence of the activity of component A(B), $a_{A(B)}$, on all the above parameters considering the nearest-neighbour atoms interaction only for B2 *four* defect, is given by

$$RT\ln a_{\mathrm{A}} = 4N[(2+\chi)h_{AA} - \chi h_{BB}] + (2-2y_A-2y_B-z)\Delta H_{AB} + (2+2\chi-2y_A+ \\ +2y_B+z)\Delta H_{A\square} - (2+2\chi-2y_A+2y_B-z)\Delta H_{B\square} + RT\left[\left(\frac{z}{2}+\chi+y_A\right)\ln 2 + \\ +\left(\frac{z}{2}+y_B+-\chi\right)\ln 2-(1+z)\ln(1+z) + y_A\ln y_A + y_B\ln y_B + \left(\frac{z}{2}-\chi+y_{\mathrm{A}}+ \\ -y_{\mathrm{B}}-1\right)\ln\left(\frac{z}{2}+\chi+y_{\mathrm{A}}-y_{\mathrm{B}}\right) + \left(\frac{z}{2}+\chi-y_{\mathrm{A}}+y_{\mathrm{B}}+1\right)\ln\left(\frac{z}{2}-\chi-y_{\mathrm{A}}+y_{\mathrm{B}}\right)+ \\ +\left(\frac{3}{2}+\chi-y_A\right)\ln(1-2\chi-2y_A)-\left(\frac{1}{2}+\chi+y_B\right)\ln(1-2y_B+2\chi)\Big] - 4NT[(2+ \\ \chi)s_{AA} - \chi s_{BB}] + T\big[(2-2y_A-2y_B-z)\Delta S_{AB} + (2+2\chi-2y_A+ +2y_B+z)\Delta S_{A\square} - \\ (2+2\chi-2y_A+2y_B-z)\Delta S_{B\square}\big] - G_A^0, \qquad (3.13a)$$

and

$$RT\ln a_B = 4N\left[\left(\chi-\frac{1}{2}\right)h_{AA} + \left(\frac{3}{2}-\chi\right)h_{BB}\right] + (1-2y_A-2y_B-z)\Delta H_{AB} + \\ -(2-2\chi+2y_A-2y_B-z)\Delta H_{A\square} + (2-2\chi+2y_A-2y_B+z)\Delta H_{B\square} - RT\Big[(1+ \\ +z)\ln(1+z)-(z+y_A+y_B)\ln 2 - y_A\ln y_A - y_B\ln y_B - \Big(1-\chi+y_A-y_B+ \\ +\frac{z}{2}\Big)\ln\left(\frac{z}{2}+\chi+y_{\mathrm{A}}-y_{\mathrm{B}}\right) + \left(1-\chi+y_A-y_B-\frac{z}{2}\right)\ln\left(\frac{z}{2}-\chi-y_{\mathrm{A}}+y_{\mathrm{B}}\right)+ \\ +\left(\frac{1}{2}-\chi+y_A\right)\ln(1-2\chi-2y_A)-\left(\frac{3}{2}-\chi-y_B\right)\ln(1-2y_B+2\chi)\Big] - 4NT\Big[\Big(2\chi+ \\ -\frac{1}{2}\Big)s_{AA} + \left(\frac{3}{2}-2\chi\right)s_{BB}\Big] + T\big[(1-2y_A-2y_B-z)\Delta S_{AB} - (2-2\chi+2y_A-2y_B+ \\ -z)\Delta S_{A\square} + (2-2\chi+2y_A-2y_B+z)\Delta S_{B\square}\big] - G_B^0 \qquad (3.13b)$$

where G_A^0 and G_B^0 are the Gibbs free energy of pure A and B, respectively, in its reference state (cf. Eq. (22) in [3]).

The relationship between z, χ and T is given by Eq. (3.12). In principle, by fitting Eq. (3.12) to the experimentally determined vacancy concentration as a function of composition at a constant temperature, the dependence of z on χ can be determined. The other way to determine $z(\chi)$ is by simultaneously fitting the enthalpy of formation and thermodynamic activity data, both as a function of composition at constant temperature. Having obtained the model parameters (note that these are ΔH_{ij} and ΔS_{ij} for the fitting of the vacancy concentration and h_{ij} and s_{ij} for

the fitting of the thermodynamic properties, respectively), the temperature dependence of the vacancy concentration can also be determined using Eq. (3.12).

The relation between z, χ and T is prescribed implicitly by Eq. (3.12). The task now is to determine $z(\chi)$ by fitting Eq. (3.12) to experimentally determined vacancy concentrations as a function of composition at a constant temperature or by simultaneous fitting the enthalpy of formation and thermodynamic activity data, both as a function of composition at constant temperature. One may also use experimental $z(T)$ data measured for constant compositions χ as input for the fitting, or a combination of all of these data sets ($z(\chi)$, $z(T)$, $\Delta H(\chi)$ and $a_B(\chi)$) as input for the fitting procedure. Details about the two fitting procedures to be applied in the future work, the 'numerical' procedure and the 'analytical' procedure, are given in the Future prospect.

As a test for the validity of our model we apply it for B2 type three defect. In this case of three defect $z_\beta = 0$ while the other defect parameters stay the same. On the other hand for B2 type structure the values of m, n and coordination number for nearest-neighbour atoms (Z) will be $m = 1$, $n = 1$ and $Z = 8$, respectively. Accordingly, the form of H from eq. (2.9) for the nearest atoms interaction only takes the form

$$H = 4N\{2y_A h_{AA} + [1 - 2y_A - 2y_B - z]h_{AB} + 2z_\beta h_{A\square} + 2z_\alpha h_{B\square} + 2y_B h_{BB}\} \quad (3.14)$$

Again from eq. (2.2b) and assumption 8 we have

$$2y_A = z - 2\chi + 2y_B \quad (3.15)$$

$$z = z_\alpha + z_\beta = z_\alpha \quad (3.16)$$

After substituting the above two equations in addition to eqs. (3.2a) and (3.2c) in to eq. (3.14) gives

$$H = 4N[(1-2\chi)h_{AB} + 2\chi h_{BB}] - 2(z - 2\chi + 2y_B)\Delta H_{AB} + 2z\Delta H_{B\square}$$

This equation is nothing but J. Breuer's result which appears in the paper [27].

CHAPTER FOUR

DISCUSSION AND CONCLUSIONS

4.1 Discussion

In this work a generalized pair interaction model of the Bragg-Williams type for binary intermetallic compounds A_mB_n composed of two sublattices and exihibiting B2, $L1_0$ and/or $L1_2$ structures is presented. In the development of the model the enthalpy and entropy of nearest- and next-nearest-neighbour atoms interaction are considered as the basic parameters. Here the entropy incorporates vibrational and configurational entropies. It is designed to describe ordered binary intermetallic compounds containing all types of point defect from the simple mono vacancy type up to the complex type of defect called hybrid (*four*). As we showed in Chapter three, it can be simplified to one of the specified structure having a certain type of point defect.

The Bragg-Williams model presented is capable of describing defect concentrations of intermetallic compounds that incorporate all four possible point defects. Using accurate experimental data for the enthalpy of formation and the thermodynamic activity, both as a function of the composition (and, if available, of the temperature) in the homogeneity range of the $A_{1-x}B_x$ compound, the model parameters for the enthalpy and the entropy of interaction terms of pairs of atoms can be determined. If, however, experimental input data are not available to a sufficient degree (as is the case for B2-$Fe_{1-x}Al_x$ that exists predominantly only on the Fe-rich side of the stoichiometric composition), the model may not lead to satisfactory results: no unique parameter set can be determined [16].

Vacancy concentrations as a function of the composition and temperature in ordered binary intermetallic compounds are parameters used to compare results between theory and experiment. A necessary step to check the validity of a model is to compare it with reliable experimental data. Before one tries to make a comparison between our model and experimental data, we would like to make a few remarks about what experimental data can fulfill this purpose. Some researchers compared their models with activity data of intermetallics. However, activity data do not appear to be very sensitive to point-defect structures, as it has been found that

different models (which predict different defect structures) gave very similar fits to activity data [27]. Therefore, comparison with activity data does not appear to be a sensitive check for a model. On the other hand, different models predict quite different composition and temperature dependences of vacancies. Thus comparison with the experimentally determined vacancy concentration as a function of the composition and the temperature can provide a critical check for theoretical models.

The model parameters for the enthalpy and the entropy of interactaction of pairs of atoms can be determined using accurate experimental data of the enthalpy of formation and the thermodynamic activity, both as a function of the composition (and, if available, of the temperature) in the homogeneous range of the $A_{1-x}B_x$ compound. If, however, experimental input data are not available to a sufficient degree the model may not lead to satisfactory results.

A comparison of the Bragg-Williams statistical thermodynamical method with methods that apply the Wagner-Schottky approximation for fitting of experimental data or methods that calculate the model parameters by ab initio approaches shows that the model parameters of the individual methods cannot be transferred into each other directly. Yet, the methods can be compared considering ”higher level parameters” as the effective enthalpy of formation of the point defects, that can be calculated assuming the usual Arrhenius-type temperature dependence of the defect concentrations. On the basis of the current evaluation of literature data, it follows that the revisited statistical method based on pair interactions provides a consistent description of important properties of intermetallic compounds.

To the best of our knowledge, up to the day the work is completed, there is no generalized Bragg-Williams model for ordered binary intermetallic compounds having a structure of B2, $L1_0$ and/or $L1_2$ with hybrid or less type of point defect. In addition, we did not see a simplified model as we did for ordered binary B2 acquiring hybrid (*four*) defect. Finally, we want to see that, if accurate experimental vacancy concentration and thermodynamic data are available, it would be straight forward to apply the model and determine thermodynamic parameters of a certain intermetallic compound.

4.2 Conclusions

A pair interaction model of the Bragg-Williams type for binary intermetallic compounds A_mB_n composed of two sublattices and exhibiting various crystal structures is presented. The model incorporates the contribution of the vibrational entropy. It is capable of describing intermetallic compounds that incorporate all four possible point defects: vacancies and antistructure atoms on both sublattices. The general model as presented can be adjusted (i.e. simplified) easily to more special cases, e.g. when certain defect types can be ignored.
An elaboration of the hybride defect types model for the thermodynamics of point defects in B2-type ordered compounds makes it possible to determine the parameters of the model not only to fit to experimentally determined vacancy concentrations, but also to experimentally determined enthalpy of formation and thermodynamic activity data.

A. Fitting to experimentally determined vacancy concentrations
– If an experimental data of good accuracy is available, fitting of the hybride defect types model to (only) experimentally determined vacancy concentrations as function of composition at constant temperature and pressure in B2-intermetallic compounds can show that the fitting procedures lead to at least as good fits of the model to the experimental data than obtained by using the values for the fit parameters as given by [21, 6]. However at the moment there is no available experimental data on which we can do fitting of theoretical and experimental vacancy concentration as a function of composition.

B. Fitting to experimentally determined enthalpy of formation and thermodynamic activity data
– Again here also if an experimental data of good accuracy is available, fitting of the hybride defect types model to (only) experimentally determined enthalpies of formation and activities in binary B2 intermetallic compounds at constant temperature and pressure can provide good description of the experimental data. However, fitting the simpler triple defect model containing less fit parameters [19] yields fits of the same good quality. Once again we want to mention that if experimental data of enthalpy of formation and activity are available fitting of theoretical and experimental enthalpy of formation and activity as a function of composition can be performed.

Note that the fitting process in part A needs to be accomplished with part B simultaneously. Because in part A an array of experimental values of vacancy concentration data

as a function of composition at a certain temperature and pressure is compared with an array of theoretical vacancy concentration to determine the enthalpy of formation. On the other hand in part B experimental value of enthalpy of formation and activity data will be compared with the theoretical enthalpy of formation and activity data to generate the array of vacancy concentration given in part A. From the above two statements, it is clear that the two fitting procedures are interrelated so that the task should be carried out self consistently for the theoretical values to match with the experimental data.

Finally, we would like to recommend that the subset of the generalized model presented in Chapter three can be modified to a more complex one by adding next-nearest, next-next-nearest, etc atoms interactions for more accurate fitting of experimental with theoretical data. In addition, the generalized model can be applied in a similar manner for $L1_0$ and $L1_2$. The same generalized model can be carried out for ternary ordered intermetallic compounds.

Future prospect

Algorithm for fitting the model equations

The z-χ-T- relationship given by Eq. (3.12) is the equation to work with when starting any of the fitting procedures presented in this work. There are two different ways of solving the implicit relationship provided by this equation: a "numerical" procedure (see 1) and an "analytical" procedure (see 2). Because of their physical meaning, Eq. (3.12) is to be fulfilled by only real (i.e. not complex) values for the ΔH_{ij}- and ΔS_{ij}- parameters, by only positive real z-values and by only real χ-values with absolute values less than 0.5. Applying Descartes' rule of signs to the polynomial Eq. (3.12), it is seen that there can be only one positive root for z that can be real or complex for every eligible χ value [27].

1 The "numerical" procedure

For the *numerical* method, z as a function of χ and T can be obtained from Eq. (3.12) numerically, for a given parameters ΔH_{AB}, $\Delta H_{A\square}$, $\Delta H_{B\square}$, ΔS_{AB}, $\Delta S_{A\square}$ and $\Delta S_{B\square}$. First an array of (real) values for the vacancy concentration z (i.e. $0 \leq z \leq 1$) is chosen. Using Eq. (3.12) for a given T, this array of z values can be transferred into an array of χ values. Then, the physically relevant χ values, i.e. the χ values pertaining to the alloys concerned, are selected. Thereby a "calculated" data set $z(\chi)$results. Clearly, this indirect procedure requires that the density of the initial z array is much larger than that of the array of experimental χ values. When performing the numerical/indirect method, there are two options for the z-χ-y_A-y_B (hybride defect model) or the z-χ-y_A-y_B (hybride defect types model) set, that is taken for the actual fitting to the experimental data of the vacancy concentration and the thermodynamic properties: one may either take the χ values that come out of the computation of Eq. (3.12) (and Eqs. (3.10) and (3.11)) or replace the calculated χ-values by the experimental ones (while keeping the z, y_A (and y_B) values corresponding to the calculated χ-values; the z values, y_A value (and y_B values) then become approximate ones.). If the fitting is carried out with a sufficiently dense array of z values, the difference in the results obtained by both options is insignificant.

For the *fitting to the measured data for the vacancy concentration z* one now calculates the difference, i.e. the error between the "calculated" $z(\chi)$ and the experimental $z(\chi)$ values. For the *fitting to the thermodynamic properties* (enthalpy of formation and thermodynamic activity values) one inserts the calculated z-χ-y_A-y_B set into Eqs. (3.4), (3.13a) and (3.13b) and compares the calculated and experimental values of the enthalpy of formation and the activity by determining the differences. For both fittings then the procedure starts again with a new set for the parameters ΔH_{AB}, $\Delta H_{B\square}$, ΔS_{AB} and $\Delta S_{B\square}$ and it is continued until the calculated differences are minimal.

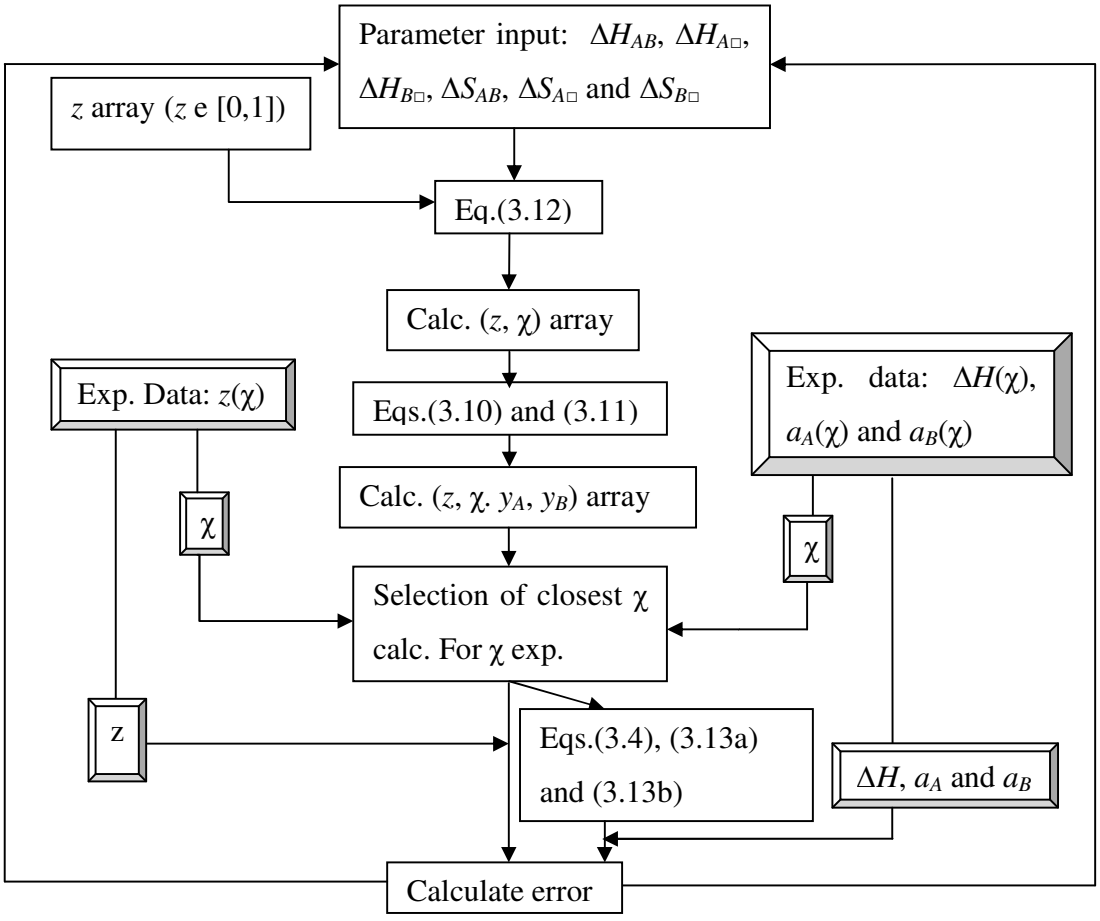

Figure 1: Scheme for the 'numerical' procedure used in the fitting of the four defect type model.

2 The "analytical" procedure

For the "analytical" procedure an appropriate mathematical software program can be used that finds *directly* extensive analytical equations for the four roots of Eq. (3.12) for z, for given parameters ΔH_{AB}, $\Delta H_{B\square}$, ΔS_{AB} and $\Delta S_{B\square}$ and a given temperature T. Inserting the experimental χ values into the equations of the four roots of Eq. (3.20) for z, the four possible z-y_B-χ arrays are computed. There can be only one positive root for z (see introduction of the Future prospect) and this root (that can be real or complex) is selected. If the root is complex, it is accepted if the imaginary part can be neglected. The fittings to the vacancy concentration or to the thermodynamic properties then proceed as described for the numerical method (see Section 1).

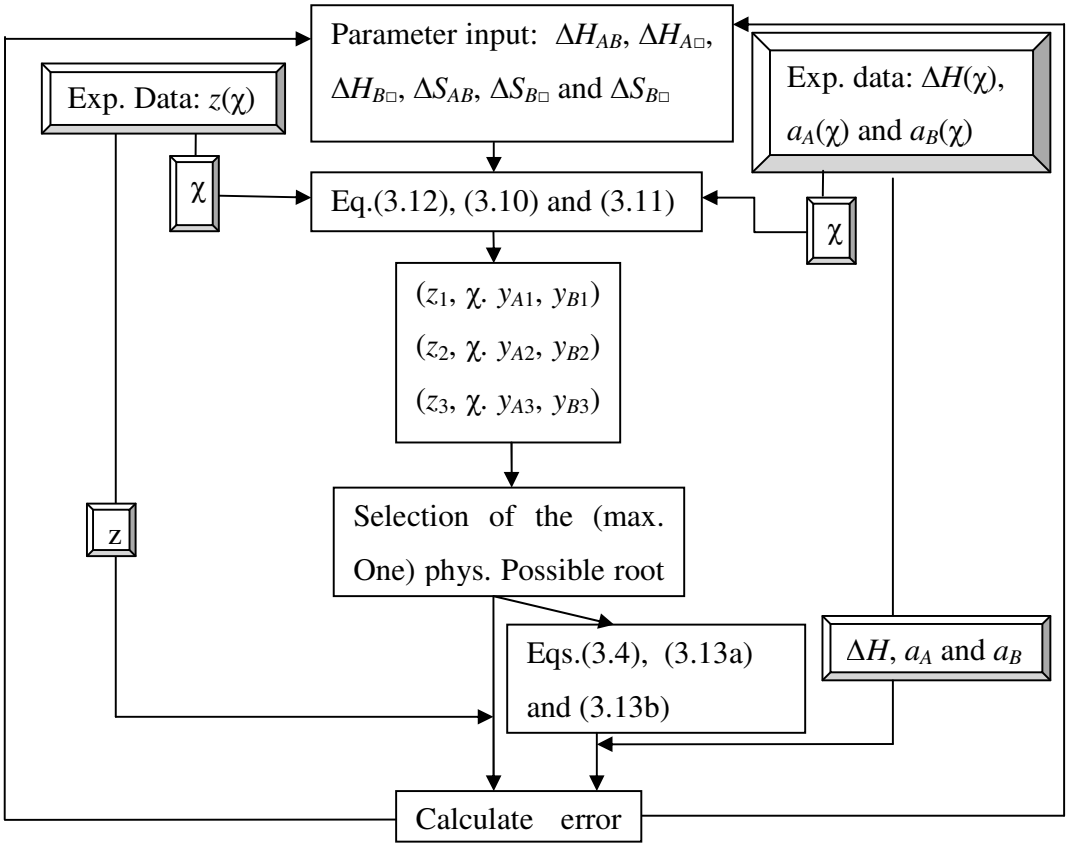

Figure 2: Scheme for the 'analytical' procedure used in the fitting of the four defect types model; see text.

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