



A unified model for point-defect formation in B2 intermetallic compounds

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[Received 26 November 1998 and accepted in revised form 16 April 1999]

ABSTRACT

With the mean-field first-nearest-neighbour interaction approximation, we derived a unified model for point defect formation in B2-structured intermetallic compounds, which accounts for all kinds of defect structures including triple-defect (TRD) type, antistructure defect (ASD) type and hybrid type. This mathematically simple model clearly manifests the physics underlying the point-defect production and defect types in intermetallics, that is the competition between two entropy production processes (ASD formation and vacancy formation) determines the type of intermetallics and defect concentrations. This model yields excellent quantitative agreement with experimental results both on the composition dependence and on the temperature dependence of vacancy concentrations for three different types of intermetallic. Based on recent experimental results and present model, we conclude that there exist no constitutional vacancies in all intermetallics including the well known NiAl, and the abnormally high vacancy concentration in such TRD compounds can be easily understood in terms of the ASD–vacancy competition. The energy barrier between the forming vacancy configuration and the ASD configuration determines three apparently different types of B2 intermetallic, and there exists no fundamental difference between three apparently different types of intermetallic. Finally, we predict firstly that the vacancy concentration is asymmetric with respect to stoichiometry for all B2 intermetallics including the ASD type and secondly that the vacancy concentration at elevated temperatures may be quite high (0.5–1%) even in ASD-type B2 intermetallics, which have been believed to contain only a negligible amount of vacancies. The physical principle of point-defect formation established in the present study for B2 intermetallics may apply to intermetallics of other structures.

§1. INTRODUCTION

In contrast with the simple vacancy formation process in pure metal and disordered alloys (Cahn and Haasen 1983), vacancy formation in intermetallic compounds (which are ordered) still remains unclear (Cottrell 1995). One unsolved but central problem 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 (Cottrell 1997). Some exhibit a very high vacancy concentration (e.g. 10%!) even at room temperature (Bradley and Taylor 1937) but have little temperature dependence (the so-called triple-defect (TRD)

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type), some contain only a small amount of vacancies but have a strong temperature dependence (the antistructure defect (ASD) type), while others are in between (called the hybrid type). This sharply contrasts the case for metals or disordered alloys, in which all different metals and disordered alloys contain only about 0.1% vacancies up to the melting temperature, and the vacancy concentration z of different metals and alloys follows a universal exponential law $z = A \exp(-E_f/RT)$, where E_f is the vacancy formation energy, A the pre-exponential efficient, R the gas constant and T the temperature. Therefore two basic but challenging questions arise.

- (1) Is it possible to give a unified and simple explanation for point-defect formation in three apparently different types of intermetallic?
- (2) What physical factors determine the defect type of a given intermetallic compound?

All the above-mentioned defect types have been found in intermetallics with the B2 (CsCl) structure; thus a convincing answer to the above questions for B2 intermetallics will provide an important basis for understanding vacancy formation in other intermetallics. Early studies considered the vacancy formation in different types of B2 intermetallic as being intrinsically different and treated them by different models. The abnormally high vacancy concentration in the TRD type was considered to be due to the presence of 'constitutional' or 'structural' vacancies (Hume-Rothery *et al.* 1952), whose existence is *energetically favourable*, in contrast with common cases. The constitutional vacancy concept explained the abnormal vacancy concentrations and the weak temperature dependence for TRD-type intermetallics such as NiAl, as modelled by Neumann *et al.* (1976) and Bakker and van Ommen (1978). On the other hand, vacancies in ASD-type intermetallics were considered to be energetically unfavourable (being similar to the case of pure metals and disordered alloys), and thus the vacancy concentration was considered to be very low but strongly temperature dependent. As a result, Ipser *et al.* (1976) proposed a model to account for the ASD formation in this type of intermetallic without considering the formation of vacancies. Then, we have two incompatible kinds of vacancy: one is the energetically favourable 'constitutional vacancies' which exist in TRD-type intermetallics; the other is the energetically unfavourable thermal vacancies which exist in ASD-type intermetallics. Obviously, the TRD type and the ASD type should be exclusive types owing to the vacancy incompatibility, and thus there should exist no hybrid type (a mixture of TRD and ASD) intermetallics (Pike *et al.* 1997). Unfortunately, there is increasing evidence showing that an in-between or hybrid type exists (Krachler *et al.* 1989, Fu 1995 and Mayer *et al.* 1995), as can be clearly seen later, and even the well known TRD intermetallics NiAl and CoAl also exhibit a slight hybridity (Kogachi and Tanahishi 1996, Kogachi *et al.* 1996). Also, many previously postulated 'ASD-type' intermetallics such as AuCd (Ren *et al.* 1997) and AgMg (Kim *et al.* 1993) turned out to exhibit a remarkably high vacancy concentration (1–3%), exhibiting a hybrid behaviour. The existence of hybrid-type intermetallics cannot be explained by TRD models or the ASD model and strongly challenges the long-standing notion of constitutional vacancies in TRD intermetallics (Ren *et al.* 1999a).

There have been a few models which tried to give a comprehensive treatment to different types of B2 intermetallic. Kim (1986, 1988) proposed a Bragg–Williams type of model which took all possible defects (vacancy on both sublattices and two kinds of ASD) into account and first pointed out that constitutional vacancies

may not necessarily exist in some TRD intermetallics, but Kim (1992) later concluded that typical TRD intermetallics such as NiAl still contain constitutional vacancies. On the other hand, a different model by Krachler *et al.* (1989) appeared to be able to reproduce various hybrid behaviours and composition dependences of vacancy concentration for different types of B2 intermetallic but seemed to be not suitable to predict the temperature dependence of defect concentrations. Despite this progress, the complexity of these models and the too many fitting parameters used (as many as four) make the physical picture behind these models not very clear. Thus the answer to the above-mentioned fundamental questions still remains obscure. It is still an open question whether constitutional vacancies exist in some intermetallics.

In the present paper we propose a unified but mathematically simple model which not only accounts for point-defect formation in different types of B2 intermetallic but also clearly manifests the physical factors governing the point-defect formation in intermetallics and the type of intermetallic. Based on the present model and recent experimental data for different types of B2 intermetallic, we shall discuss whether or not constitutional vacancies are necessary in B2 intermetallics. Finally, we shall make some predictions based on our model, which can be future tests for the validity of the model.

§2. MODEL

Let us consider an arbitrary B2 intermetallic compound with composition $A_{0.5-x}B_{0.5+x}$, where x designates the deviation from stoichiometry and it also represents the composition of intermetallics. B2 structure is characterized by two distinct sublattices, namely the α sublattice and β sublattice, which are predominantly occupied by A atoms and B atoms respectively. Because of the distinction between two kinds of sublattice site, there exist four kinds of possible point defect in principle: wrong atom on α site (B-antistructure defect (B-ASD)), wrong atom on β site (A-antistructure defect (A-ASD)), vacancy on α site (A-vacancy), and vacancy on β site (B-vacancy). We follow Neumann *et al.* (1976) to define the concentration of four kinds of point defect, because such a definition has the advantage of greatly simplifying mathematical derivation and yielding a mathematically elegant model:

$$\begin{aligned}
 y_A &= \frac{N_A^\beta}{N} && \text{(A-ASD concentration),} \\
 y_B &= \frac{N_B^\alpha}{N} && \text{(B-ASD concentration),} \\
 z_\alpha &= \frac{N_V^\alpha}{N} && \text{(A-vacancy concentration),} \\
 z_\beta &= \frac{N_V^\beta}{N} && \text{(B-vacancy concentration),}
 \end{aligned}$$

where $N = N_A + N_B$ is the total number of A and B atoms, being 1 mol atom; N_I^δ designates the number of I (=A, B, vacancy) species on the δ ($=\alpha, \beta$) sublattice. The total vacancy concentration z is given by the sum of z_α and z_β :

$$z = z_\alpha + z_\beta.$$

Obviously, the concentrations of these defects are dependent on both the composition x and the temperature T . Then the problem that we face is how to evaluate

the concentrations of these defects as a function of the composition and temperature in terms of some physical parameters (as few as possible) which characterize the intermetallic compound concerned. If the parameters used do not clearly characterize the compound concerned or do not have a clear physical meaning, modelling will become no more than a mathematical fitting process, and such models cannot give a clear physical picture of point-defect formation in intermetallics. As will be shown in the following, the present model uses three energy parameters (which can be reduced to two in most cases) with a clear physical meaning and characterizing the compounds concerned. As the result, the physical picture of point-defect formation in B2 intermetallics will be clearly manifested.

Now we adopt the first-nearest-neighbour (1NN) pairwise atomic interactions approach to calculate the free energy of the B2 intermetallic compound containing four kinds of point defect and then use the free-energy minimal condition to calculate the concentrations of these defects. Throughout the derivation, we utilize the mean-field (Bragg–Williams) approximation, that is the short-range order effect is not considered. This approach is similar to that of Neumann *et al.* (1976), but we do not follow their TRD assumption: $y_B \equiv 0$ and $z_\beta \equiv 0$. This enables us to treat all different types of intermetallic. It is important to remember that the ordered nature of B2 intermetallics imposes an important condition on the formation of point defects; the two distinct sublattices must maintain equal number of site, as demanded by the structure (Wasilewski 1968). This means that an increase in site number in one sublattice must be compensated by the same increase in the other. Another obvious condition exists, that is the formation of point defects does not alter the total number of atoms. Using the above two conditions, we can calculate the partition of A and B atoms and vacancies in the α and β sublattices as a function of defect concentrations z , y_A , y_B , z_α and z_β and the composition x , as shown in table 1. The equal-site-number condition gives the following relationships between defect concentrations (i.e. the sum of A, B and vacancies in the α sublattice must equal half the total site number, and the same applies to the β sublattice):

$$2z_\alpha = z + 2y_A - 2y_B + 2x, \quad (1a)$$

$$2z_\beta = z - 2y_A + 2y_B - 2x. \quad (1b)$$

Owing to the existence of the two relations (1a) and (1b) between five unknowns z , y_A , y_B and z_α and z_β , there are three independent variables to be determined. The relationship between the four kinds of point defect can be obtained by subtracting equation (1b) from equation (1a):

$$z_\alpha - z_\beta = 2y_A - 2y_B + 2x. \quad (1')$$

Table 1. Partition of A and B atoms and vacancies in the two sublattices of B2 intermetallics.

Species	α sublattice	β sublattice	Total
A	$N_A^\alpha = (N/2)(1 - 2y_A - 2x)$	$N_A^\beta = (N/2)2y_A$	$N_A = (N/2)(1 - 2x)$
B	$N_B^\alpha = (N/2)2y_B$	$N_B^\beta = (N/2)(1 - 2y_B + 2x)$	$N_B = (N/2)(1 + 2x)$
Vacancy	$N_V^\alpha = (N/2)2z_\alpha$	$N_V^\beta = (N/2)2z_\beta$	$N_V = (N/2)2z$
$N_A + N_B + N_V$	$N^\alpha = (N/2)(1 + z)$	$N^\beta = (N/2)(1 + z)$	$N_{\text{site}} = N(1 + z)$

With the partition of atoms and defects shown in table 1, we can calculate the number of six kinds of nearest-neighbour atomic bonds, AA, BB, AB, BV (V means vacancy), AV and VV, by using the mean-field approximation. Assuming that $x \ll 1$, $z_\alpha \ll 1$, $z_\beta \ll 1$, $y_A \ll 1$ and $y_B \ll 1$, we can neglect terms higher than first order of these quantities during calculation. The number of these atomic bonds are thus given by

$$\begin{aligned} n_{AA} &= Z(N_A^\beta C_A^\alpha) = 4N(2y_A), \\ n_{BB} &= Z(N_B^\alpha C_B^\beta) = 4N(2y_B), \\ n_{AB} &= Z(N_A^\alpha C_B^\beta + N_B^\alpha C_A^\beta) = 4N(1 - 2y_A - 2y_B - z), \\ n_{BV} &= Z(N_V^\alpha C_B^\beta + N_B^\alpha C_V^\beta) = 4N(z + 2y_A - 2y_B + 2x), \\ n_{AV} &= Z(N_A^\alpha C_A^\beta + N_A^\alpha C_V^\beta) = 4N(z - 2y_A + 2y_B - 2x), \\ n_{VV} &= Z(N_V^\alpha C_V^\beta) = 0, \end{aligned}$$

where C_I^δ ($I = A, B, V; \delta = \alpha, \beta$) 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: $N^\delta = (N/2)(1 + z)$. $Z = 8$ is the coordination number of B2 structure.

Let AA, BB, AB, BV, AV and VV bonds have bond energies u_{AA} , u_{BB} , u_{AB} , u_{BV} , u_{AV} and u_{VV} respectively; now we are able to express the internal energy U in terms of defect concentrations;

$$\begin{aligned} U &= n_{AA}u_{AA} + n_{AB}u_{AB} + n_{BB}u_{BB} + n_{AV}u_{AV} + n_{BV}u_{BV} + n_{VV}u_{VV} \\ &= 4N[u_{AB} + 2x(u_{BV} - u_{AV})] + [-(2y_A + 2y_B + z)\Delta H_{AB} \\ &\quad + (z - 2y_A + 2y_B)\Delta H_{AV} + (z + 2y_A - 2y_B)\Delta H_{BV}], \end{aligned} \quad (2)$$

where

$$\Delta H_{AB} = 4N \left(u_{AB} - \frac{u_{AA} + u_{BB}}{2} \right),$$

is the ordering energy of the stoichiometric compound,

$$\Delta H_{BV} = 4N \left(u_{BV} - \frac{u_{BB}}{2} \right),$$

$$\Delta H_{AV} = 4N \left(\frac{u_{AV} - u_{AA}}{2} \right).$$

The physical meaning of the latter two parameters will be discussed later.

The configurational entropy is given by

$$\begin{aligned} S &= k \ln \left(\frac{N^\alpha!}{N_A^\alpha! N_B^\alpha! N_V^\alpha!} \frac{N^\beta!}{N_A^\beta! N_B^\beta! N_V^\beta!} \right) \\ &= k \frac{N}{2} [2(1 + z) \ln(1 + z) - (2y_A) \ln(2y_A) - (2y_B) \ln(2y_B) \\ &\quad - (1 - 2y_A - 2x) \ln(1 - 2y_A - 2x) - (1 - 2y_B + 2x) \ln(1 - 2y_B + 2x) \\ &\quad - (z + 2y_A - 2y_B + 2x) \ln(z + 2y_A - 2y_B + 2x) \\ &\quad - (z - 2y_A + 2y_B - 2x) \ln(z - 2y_A + 2y_B - 2x)]. \end{aligned} \quad (3)$$

Then the free energy of the defect configuration is expressed by $F = U - TS$. Minimizing the free energy with respect to three independent variables z , y_A and y_B , that is $\partial F/\partial z = 0$, $\partial F/\partial y_A = 0$ and $\partial F/\partial y_B = 0$, yields the following equations (after some manipulation) which governs point-defect formation in B2 intermetallics:

$$4 \Delta H_{AB} = RT \ln(4y_A y_B), \quad (4a)$$

$$4 \Delta H_{BV} = RT \ln \left(\frac{y_B}{2z_\alpha^2} \right), \quad (4b)$$

$$4 \Delta H_{AV} = RT \ln \left(\frac{y_A}{2z_\beta^2} \right). \quad (4c)$$

Of the four defect concentrations y_A , y_B , z_α and z_β , there are only three independent variables (because of the existence of relation (1')). They can be uniquely determined by the three energy parameters ΔH_{AB} , ΔH_{BV} and ΔH_{AV} . Therefore, equations (4) act as the master equations governing point-defect formation in B2 intermetallics.

Now we can simplify the above equations by considering a more practical situation. If ΔH_{BV} and ΔH_{AV} differ very much (we shall later show that it is almost always the case), say, $\Delta H_{AV} \gg \Delta H_{BV}$, we can prove that $z_\alpha \gg z_\beta$. It means that vacancies predominantly occupy one sublattice (the α sublattice), leaving the other sublattice (the β sublattice) nearly free of vacancies, that is $z_\beta \approx 0$ and thus $z \approx z_\alpha$. In this case, the three independent variables reduce to two; thus it is possible to use equations (4a) and (b) to describe such a situation. Using equation (1') and $z_\beta = 0$, we obtain a more convenient form

$$4 \Delta H_{AB} = RT \ln [2y_B(z + 2y_B - 2x)], \quad (5a)$$

$$4 \Delta H_{BV} = RT \ln \left(\frac{y_B}{2z^2} \right), \quad (5b)$$

in which two energy parameters ΔH_{AB} and ΔH_{BV} completely determine the composition dependence and temperature dependence of the two independent defect concentrations, namely the vacancy concentration $z (= z_\alpha)$ and the B-ASD concentration y_B , (the A-ASD concentration y_A can be calculated using equation (1')). We shall show later that the simplified equations (equations (5a) and (5b)) give excellent agreement with experimental results for all kinds of B2 intermetallic. This implies that the assumption $z_\alpha \gg z_\beta$ appears valid for all kinds of B2 intermetallic compound. A justification of this assumption will be given below by considering the fundamental feature of intermetallics. Compared with previous models (Kim 1986, 1988, Krachler *et al.* 1989), our model is in a very simple form.

Although equations (5a) and (5b) are simple in mathematical form, they are not convenient for calculation, because the defect concentrations z and y_B are implicit functions of the composition x and temperature T . Fortunately, as can be easily derived from equations (5a) and (5b), x can be written as explicit functions of z , y_B and T as follows:

$$x = \frac{1}{2} \left[z + 4z^2 \exp \left(\frac{4 \Delta H_{BV}}{RT} \right) - \frac{1}{4z^2} \exp \left(\frac{4 \Delta H_{AB} - 4 \Delta H_{BV}}{RT} \right) \right], \quad (5a')$$

$$x = \frac{1}{2} \left[2y_B + \left(\frac{y_B}{2} \right)^{1/2} \exp \left(-\frac{2 \Delta H_{BV}}{RT} \right) - \frac{1}{2y_B} \exp \left(\frac{4 \Delta H_{AB}}{RT} \right) \right]. \quad (5b')$$

Equations (5a') and (5b') are convenient for calculations. Equation (5a') can be used to make a best fitting to the experimental vacancy concentrations and to obtain the energy parameters ΔH_{AB} and ΔH_{BV} . Equation (5b') can be used to calculate the B-ASD concentration y_B as a function of the composition parameter x and the temperature T . The A-ASD concentration can be calculated from equation (1') using the assumption $z = z_\alpha (z_\beta = 0)$.

§3. THE PHYSICAL MEANING OF THE ENERGY PARAMETERS ΔH_{AV} AND ΔH_{BV}

Of the three energy parameters ΔH_{AB} , ΔH_{BV} and ΔH_{AV} in equations (4a), (4b) and (4c) which determine the point-defect formation in B2 intermetallics, ΔH_{AB} has a well defined physical meaning, the ordering energy of intermetallic compound. Some studies (Neumann *et al.* 1976, Neumann 1980) used the formation energy of intermetallics as the ordering energy; however, it should be pointed out that 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.

In the following we discuss the physical meaning of the remaining two energy parameters, namely ΔH_{BV} and ΔH_{AV} . We consider the problem of how to compensate the off-stoichiometry in B2 intermetallics at 0 K. In this case, we have an equal number of α - and β -sublattice sites, but unequal numbers of A and B atoms. Obviously, point defects must be created even at 0 K because only stoichiometric compound can be free of point defects at 0 K.

On the B-rich side ($x > 0$), there exist two ways to compensate the off-stoichiometry (Wasilewski 1968). One way is to form B-ASDs on the α site without vacancy formation. In this case we have $y_B = x$, $y_A = 0$ and $z = z_\alpha = 0$. The other way is to form two A vacancies on the α site while leaving all B atoms in their own sublattice β ; in this case we have $z = z_\alpha = 2x$, $y_B = 0$ and $y_A = 0$. Therefore, vacancy compensation produces twice the number of point defects that ASD compensation does, as a result of the equal-sublattice-sites constraint. Then the energy difference between forming A vacancies with concentration $2x$ and B-ASD on the α sublattice with concentration x can be calculated by substituting the above conditions respectively into equation 2 and subtracting. The result is

$$U_{A\text{-vac}}^\alpha - U_{B\text{-ASD}}^\alpha = 4x \Delta H_{BV}, \quad (6a)$$

where $U_{A\text{-vac}}^\alpha$ and $U_{B\text{-ASD}}^\alpha$ are the internal energies for the A-vacancy (on the α -sublattice) configuration and B-ASD (on the α -sublattice) configuration respectively at 0 K. From the above relation, we can clearly see that ΔH_{BV} characterizes the energy barrier between vacancy accommodation and ASD accommodation for the off-stoichiometry on the α sublattice (the subscript B means B-ASD in the α sublattice, and the subscript V means vacancy in the α sublattice).

By the same argument, on the A-rich side of stoichiometry ($x < 0$), we find the energy difference between the B-vacancy accommodation and A-ASD accommodation (with a vacancy concentration twice the ASD concentration) on the β sublattice at 0 K can be expressed by

$$U_{B\text{-vac}}^\beta - U_{A\text{-ASD}}^\beta = 4|x| \Delta H_{AV}. \quad (6b)$$

Thus ΔH_{AV} characterizes the energy barrier at 0 K between vacancy accommodation and ASD accommodation for off-stoichiometry on the β sublattice (the subscript A

means an A-ASD in the β sublattice, and the subscript V means a vacancy in the β sublattice).

If either of the two quantities ΔH_{BV} and ΔH_{AV} is negative, it means that vacancy configuration is more stable than ASD configuration at 0 K, that is these vacancies are constitutional vacancies. If both are positive, no constitutional vacancies exist, and they reflect the relative energy disadvantage of forming a vacancy configuration over forming ASD configuration.

Now we evaluate the relative values of ΔH_{BV} and ΔH_{AV} , because this result is important for the validity of the simplified equations (5a) and (5b). Since we have understood the physical meaning of these energy parameters, it is not difficult to give a qualitative evaluation by simply considering the factors affecting these quantities. The two distinct sublattices of B2 intermetallics make a marked difference in the tendency to form vacancies and ASDs. This is because the two sublattices are occupied predominantly by two completely different atoms A and B, which have different atomic sizes and chemical affinities. Even from a simple atomic size consideration (Fu *et al.* 1993), it is easy to understand that in one sublattice site (the smaller one, say, A) it is easy to introduce a vacancy but difficult to introduce an ASD, while in the other sublattice (the larger one, say B) it is difficult to introduce a vacancy but easy to introduce an ASD. Therefore, according to the physical meanings of ΔH_{BV} and ΔH_{AV} , the former sublattice has a small energy barrier ΔH_{BV} and the latter sublattice has a large energy barrier ΔH_{AV} . Therefore, there should be a large difference between ΔH_{BV} and ΔH_{AV} even from simply considering the atomic size factor alone. Other differences between the two sublattices should have a similar effect, that is should make a large difference between ΔH_{BV} and ΔH_{AV} . This difference is expected to be even larger for strongly ordered intermetallics such as NiAl and CoAl, where there are large differences in atomic sizes and chemical affinities.

The above argument gives a qualitative justification of the assumption made in the previous section that there is a large difference between ΔH_{BV} and ΔH_{AV} . In most of this paper we assume that $\Delta H_{BV} \ll \Delta H_{AV}$ (i.e. it is difficult to form a vacancy on the β sublattice). We shall see later that the simplified master equations (5a) and (5b) using this assumption gives excellent agreement with not only strong intermetallics such as NiAl, but also weak intermetallics such as AuCd. Therefore, we expect this condition to be satisfied in almost all B2 intermetallics.

§4. THE PHYSICAL PICTURE OF THE PRESENT MODEL; THE PRINCIPLE OF POINT-DEFECT FORMATION IN INTERMETALLICS

The simple form of our model (equations (4)) and the clear physical meaning of the energy parameters used enable us to give a simple picture of the point-defect formation in B2 intermetallics, and this picture may be true for other intermetallics as well.

There are two distinct sublattices in B2 intermetallics. A basic way to produce point defects is to create disorder by introducing B-ASDs in the α sublattice and A-ASDs in the β sublattice. Obviously this process is controlled by the ordering energy ΔH_{AB} , as clearly manifested by equation (4a). However, there also exist two competing processes of point-defect formation in the two sublattices, as shown in the previous section. In the α sublattice, the formation of A vacancies competes with the formation of B-ASDs. In the β sublattice, the formation of B vacancies competes with the formation of A-ASDs. These are clearly reflected by equations (4b) and (4c) respectively. Equation (4b) shows that the A-vacancy concentration z_α relative to the

B-ASD concentration y_B is determined by the vacancy-ASD energy barrier ΔH_{BV} in the α sublattice and equation (4c) shows that the B-vacancy concentration z_B relative to the A-ASD concentration y_A is determined by the vacancy-ASD energy barrier ΔH_{AV} in the β sublattice. Therefore, our model, which is simple in mathematical form, gives a clear physical picture of the formation of point defects in B2 intermetallics. We expect that this physical picture is common to all other intermetallics with different structure, and the competition between ASD and vacancy formation can be considered to be a general principle governing the formation of point defects in all intermetallics.

We can clearly see that there exists a great difference between defect formation in disordered alloys and in ordered alloys (intermetallics). In metals and disordered alloys, which are characterized by a simple lattice, there exists no statistical distinction between different lattice sites, and in this case the only way to increase the entropy as a response to temperature increase is to form vacancies. On the other hand, in ordered intermetallics, which consist of distinct sublattices, there are two ways to produce point defects in the two sublattices in order to increase entropy: one is to form ASDs, and the other is to form vacancies. Because vacancy accommodation produces more defects than ASD accommodation does, the vacancy configuration tends to become favoured with increasing temperature from entropy consideration. Thus a large amount of vacancies may be produced at elevated temperatures if the vacancy-ASD barrier ΔH_{BV} is low. This is the case for near-TRD intermetallics such as NiAl. If the vacancy-ASD energy barrier is high, the vacancy concentration is low even at high temperatures. This is the case for near-ASD intermetallics. Similarly, the intermediate vacancy-ASD barrier gives rise to an intermediate or hybrid behaviour. Therefore, the vacancy-ASD competition can lead to various, apparently different point-defect structures in intermetallics. This is the fundamental reason why B2 intermetallics exhibit various, apparently different defect structures.

Because there is a large difference between ΔH_{BV} and ΔH_{AV} (let us take $\Delta H_{BV} \ll \Delta H_{AV}$), as discussed in the previous section, there is a large energy barrier between the forming vacancy and the A-ASD in the β sublattice. Thus it is difficult to form vacancies in the β sublattice. Consequently, we only need to consider vacancy formation in the α sublattice. This simplified but practical situation is clearly manifested by the simplified equations (5a) and (5b). In the following section we shall use the simplified equations to make calculations and to compare with experimental results.

§ 5. VACANCY CONCENTRATIONS AS A FUNCTION OF THE COMPOSITION AND TEMPERATURE IN B2 INTERMETALLICS OF DIFFERENT TYPES: A COMPARISON BETWEEN THEORY AND EXPERIMENTAL RESULTS

A necessary step to check the validity of a model is to compare with reliable experimental data. Before making a comparison between our model and experimental data, we would like to make a few remarks about what experimental data can fulfil 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 (Krachler *et al.* 1989). 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.

Because the vacancy concentration is rather high in B2 intermetallics, it can be determined by a combination of lattice parameter measurement and macroscopic density measurement. In this kind of measurement, the major error is due to the error in macroscopic density, because the lattice parameter can be accurately determined by X-ray diffraction. The existence of microvoids in the samples (which are introduced during solidification of the melt into polycrystals) gives a systematic error to the macroscopic density, leading to an overestimation of the vacancy concentration (van Ommen *et al.* 1981). This problem is very serious on the vacancy-rich side of stoichiometry owing to the pronounced increase in microvoids. As a consequence, some of the early data might have overestimated the vacancy concentration by 1% for the vacancy-rich side of stoichiometry (Kim 1992). Being aware of this problem, Kogachi and Tanahishi (1996), Kogachi *et al.* (1996) and Kogachi and Haraguchi (1997) have recently performed careful experiments to re-evaluate the vacancy concentrations in NiAl, CoAl and FeAl, by using powdered samples with a careful chemical analysis. Their vacancy concentration data are lower than the previously reported values (Taylor and Doyle 1972, Meyer *et al.* 1976) on the vacancy-rich side. In view of the microvoid problem, we consider their results to be more reliable than previously reported values. Therefore, in the following we mainly used the data of Kogachi and co-workers (NiAl, CoAl and FeAl) to compare with our model. We also use our recent vacancy data on single-crystal AuCd (single-crystal samples do not form microvoids in principle and thus give more reliable vacancy concentrations than polycrystalline samples do). Since NiAl, CoAl, FeAl and AuCd are thought to be different types of intermetallic (NiAl and CoAl are thought to be the TRD type, FeAl to be the hybrid type and AuCd to be the ASD type), a comparison with these different types of intermetallic will provide a critical check of the generality of our model.

5.1. Composition dependence of the vacancy concentration and the non-existence of constitutional vacancies

From equation (5a'), we can use two energy parameters ΔH_{AB} and ΔH_{BV} to calculate the composition parameter dependence of vacancy concentrations at different temperatures. Different combination of the two energy parameters gives a variety of composition dependences as shown in figures 1(a)–(e), where figures 1(a), (b), (c) and (d) give the best fit to the experimentally measured composition dependence of the vacancy concentration for NiAl, CoAl, FeAl and AuCd respectively. The best-fit energy parameters ΔH_{AB} and ΔH_{BV} are listed in table 2. It can be seen that the present model gives an excellent fit to B2 intermetallics of different types. It should be noted that the vacancy concentrations measured at room temperature for furnace-cooled NiAl, CoAl and AuCd correspond to the values at the diffusion freezing temperature (approximately $(0.4\text{--}0.5)T_m$, where T_m is the melting point).

From the above fitting, we can reach several important conclusions. Firstly, from table 2, we can see that all different types of intermetallic possess a positive ΔH_{BV} . Since ΔH_{BV} represents the energy barrier between vacancy accommodation and B-ASD accommodation in the α sublattice, positive ΔH_{BV} for all types of B2 intermetallic clearly manifests that vacancy accommodation is energetically unfavourable

at 0 K for all intermetallics, that is *no 'constitutional vacancy' or 'structural vacancy' exists in B2 intermetallics*. Constitutional vacancies are also unlikely to exist in other intermetallics (such as $L1_0$, $L1_1$ and $D0_{22}$) because these compounds do not contain a high vacancy concentration (the reason will be given later). Secondly, there exists no clear boundary between different types of intermetallic, as can be seen in figure 1. The so-called TRD compounds NiAl and CoAl exhibit hybridity to some extent (i.e. below the BT line), and the so-called ASD-type AuCd exhibits a rather high vacancy concentration (about 1.5% on the Cd-rich side) and thus also shows a hybrid behaviour. This is, in fact, very natural from the present model because our model gives a unified picture for all B2 intermetallics, and thus no fundamental difference between different types is expected. Thirdly, the so-called ASD type B2 intermetallics (e.g.

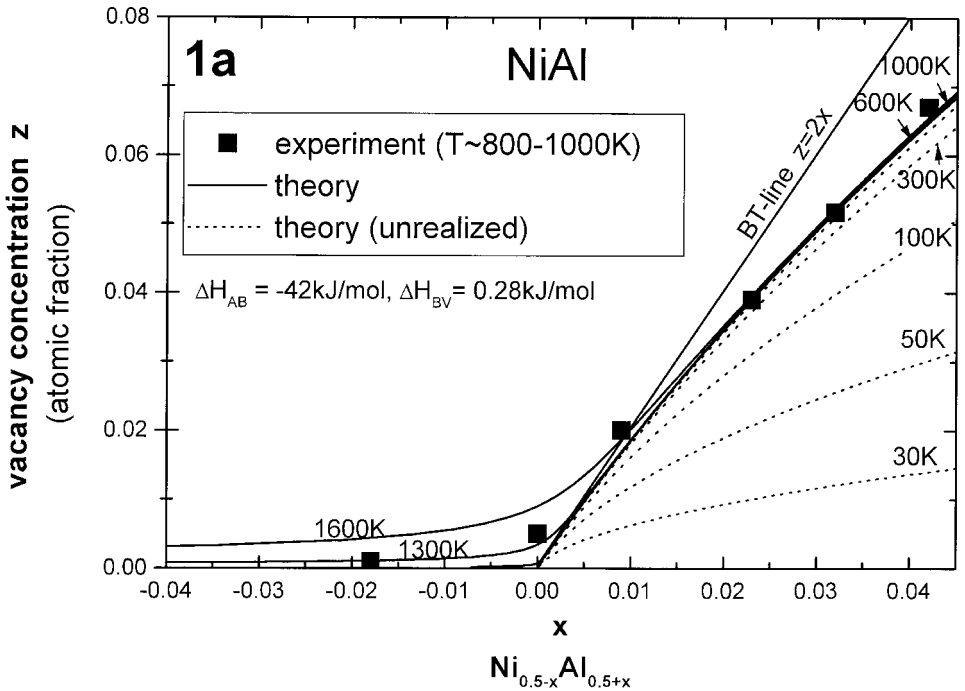


Figure 1. Comparison between experimental and calculated composition x dependences of the vacancy concentration for various B2 intermetallics, where the Bradley–Taylor (BT) line $z = 2x$ is the lower limit for true TRD behaviour (i.e. constitutional vacancies) to exist (Kogachi and Tanahashi 1996, Kogachi *et al.* 1996): (a) NiAl, experimental data from Kogachi *et al.* (1996); (b) CoAl, experimental data from Kogachi and Tanahashi (1996); (c) FeAl, data are from Kogachi and Haraguchi (1997, 1998) (open symbols), from Yang and Baker (1998) (open symbols with a vertical bar) and from Ho and Dodd (1978) (full symbols). Ho and Dodd (1978) measured the vacancy increment above the frozen-in portion; thus the total vacancy concentrations are given by adding their data to the frozen-in portion given by Kogachi and Haraguchi (1997); (d) AuCd, experimental data from Ren *et al.* (1997); (e) calculated vacancy concentration for a near-ASD-type intermetallic, no experimental data available. Theoretical vacancy concentrations below the diffusion freezing temperature ($(0.4-0.5)T_m$) cannot be realized experimentally, and they are shown as broken curves. Theoretical values above the freezing temperature are shown as solid curves, and they can be realized experimentally.

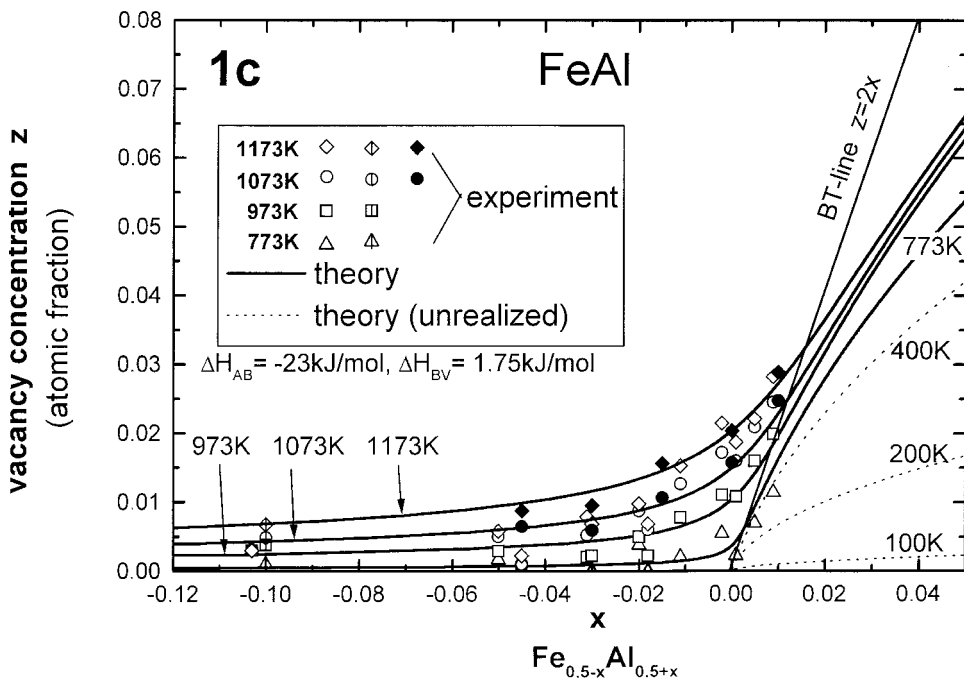
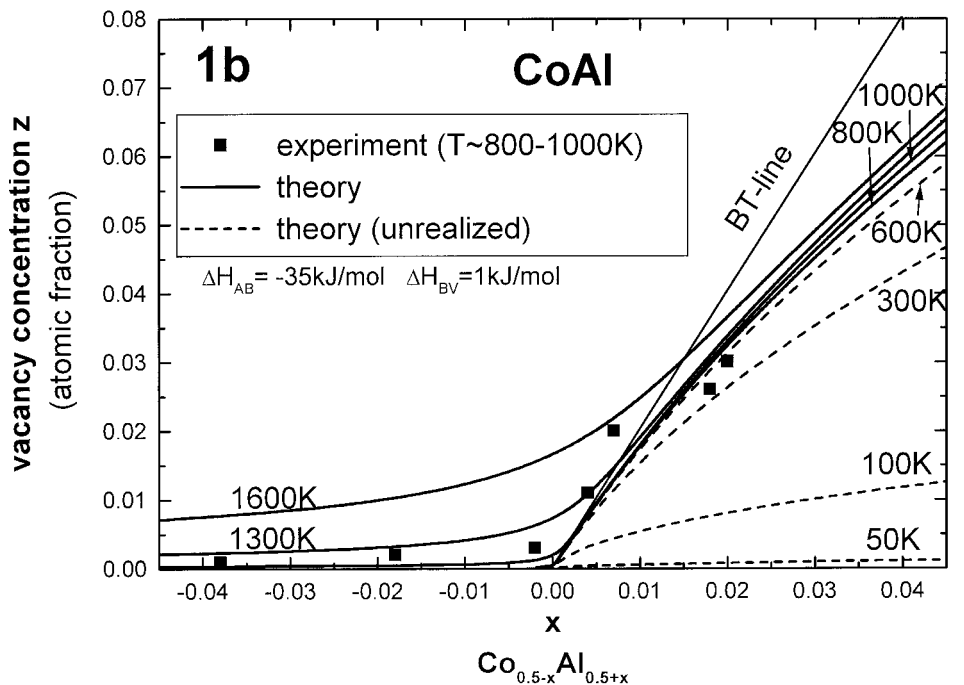


Figure 1. Continued.

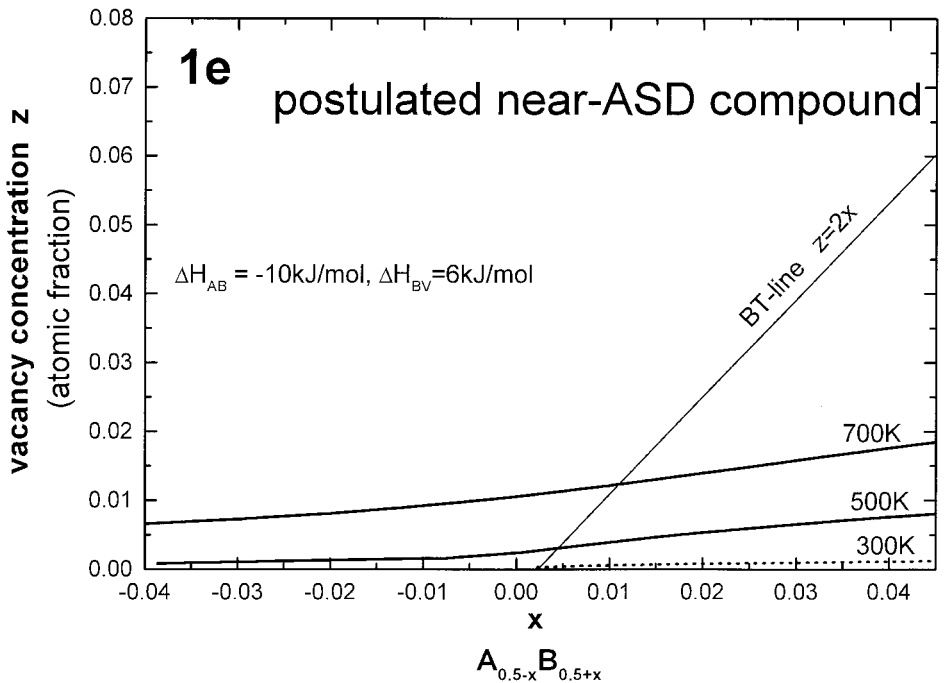
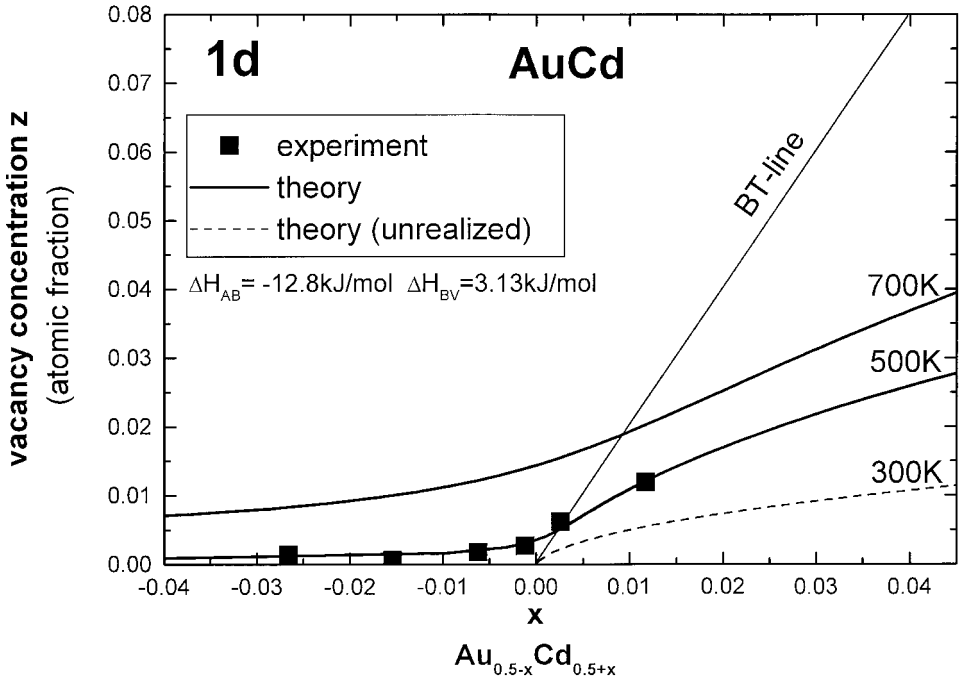


Figure 1. Continued.

Table 2. Relationship between the ordering energy ΔH_{AB} and the vacancy–ASD energy barrier ΔH_{BV} . It is clear that there is no clear boundary between ‘different’ types of compound, as indicated by the present classification of defect types. Previous classification by Neumann (1980) is also included for comparison.

Intermetallics	ΔH_{AB} (kJ mol ⁻¹)	ΔH_{BV} (kJ mol ⁻¹)	Defect type	
			Previous classification	New classification
NiAl (figure 1 (a))	-42.0	0.28	TRD type	Near-TRD type
CoAl (figure 1 (b))	-35.0	1.00	TRD type	Near-TRD type
FeAl (figure 1 (c))	-23.0	1.75	TRD type	Hybrid type
AuCd (figure 1 (d))	-12.8	3.13	ASD type	Hybrid type
Postulated (figure 1 (e))	-10.0	6.00	ASD type	Near-ASD type

AuCd), which have been generally regarded as containing a negligible amount of vacancies, may contain a fairly large amount of vacancies (about 1%). Fourthly, ΔH_{BV} increases with decreasing ordering energy $|\Delta H_{AB}|$, that is, the larger the ordering energy (absolute value), the smaller is the vacancy–ASD energy barrier, as can be seen from table 2. This suggests that intermetallics with a high ordering energy (strong intermetallics) have a smaller vacancy–ASD energy barrier ΔH_{BV} ; thus this type of intermetallic contains a very large amount of vacancies on one side of stoichiometry at elevated temperatures. On the other hand, intermetallics with a low ordering energy (weak intermetallics) have a large ΔH_{BV} ; thus such intermetallics contain a relatively small amount of vacancies. This result is quite natural if one understands the meaning of the energy parameters. Because the ordering energy reflects the difficulty of forming ASDs, if the formation of ASDs is difficult, U_{B-ASD}^{α} is increased and ΔH_{BV} decreases according to equation (6 a). Therefore, vacancy formation becomes easier in this case. This gives a simple explanation for the interesting finding by Neumann (1980) that a high ordering energy favours the formation of TRD compounds (high vacancy concentration), and a low ordering energy favours the formation of ASD compounds.

Despite the fact that there exists no fundamental difference between TRD, hybrid and ASD types, which have previously thought to be formed owing to different mechanisms, here we still try to keep this classification scheme but with some modifications. Considering that no true TRD and true ASD behaviours are expected, we can roughly classify B2 intermetallics into near-TRD, hybrid and near-ASD types. In this classification scheme, strong intermetallics such as NiAl and CoAl are classified as near-TRD type (figures 1 (a) and (b)), moderately strong intermetallics such as FeAl and AuCd can be classified into hybrid-type (figures 1 (c) and (d)), and weak intermetallics (weaker than AuCd) may be classified into near-ASD type (figure 1 (e)). However, it is obvious that such a classification is merely a rough division of a continuous spectrum.

Here we would like to make a few remarks about the current problems with experimental vacancy data measured by a combination of density measurement and lattice parameter determination. From our experience in making single-crystal and polycrystalline AuCd samples (Ren *et al.* 1997), we found that polycrystalline samples (especially for those containing large amount of vacancies) contain not only many large voids but also a large number of microvoids. These microvoids may still remain in the samples even after the samples are ground into powders of a few tens

of microns in size. This causes an appreciable overestimation of the vacancy concentration, as found in AuCd (Ito *et al.* 1999). On the other hand, in single-crystal samples, no large voids are found, and the microvoids are greatly reduced. These facts indicate that it is most desirable to use single-crystal samples to measure the vacancy concentrations. However, this was done only for AuCd (Ren *et al.* 1997; Ito *et al.* 1999). We strongly recommend that such experiments be done for the 'TRD compounds' NiAl, CoAl, etc. It is likely that such experiments will give lower vacancy concentrations than existing data, which were obtained from powdered polycrystalline samples. Such result may further support the non-existence of constitutional vacancies even in TRD compounds.

5.2. Temperature dependence of the vacancy concentration

Figures 2 (a), (b) and (c) show the calculated temperature dependences of the vacancy concentration (from equation (5 a')) for near-TRD type NiAl, hybrid-type FeAl and a postulated near-ASD-type intermetallic compound (behaving as figure 1 (e)). They are characterized as follows: in figure 2 (a) by a large ΔH_{AB} and a small ΔH_{BV} ; in figure 2 (b), by an intermediate ΔH_{AB} and an intermediate ΔH_{BV} ; in figure 2 (c) by a small ΔH_{AB} and a large ΔH_{BV} . These energy parameters have been determined in figure 1, as listed in table 2. Experimental data on NiAl and FeAl

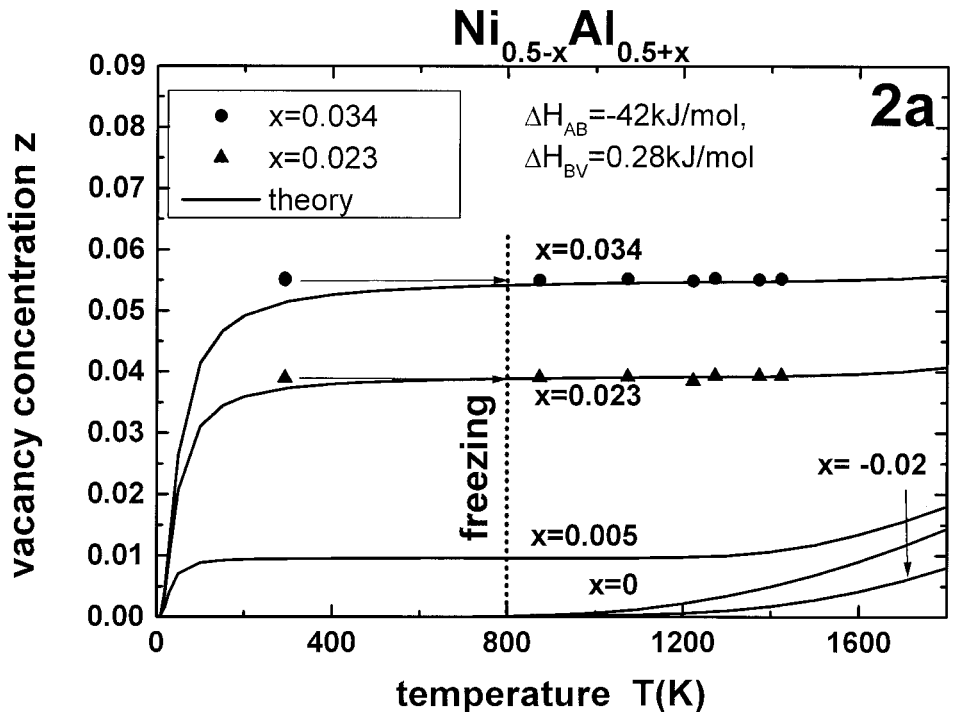


Figure 2. Comparison between the experimental and the calculated temperature dependences of vacancy concentration for three different types of B2 intermetallic: (a) near-TRD-type NiAl, experimental data from Kogachi *et al.* (1995, 1996); (b) hybrid-type FeAl, experimental data from Kogachi and Haraguchi (1997) (full squares and full triangles) and Yang and Baker (1998) (full circles); (c) calculated near-ASD intermetallics, no experimental data available for a comparison.

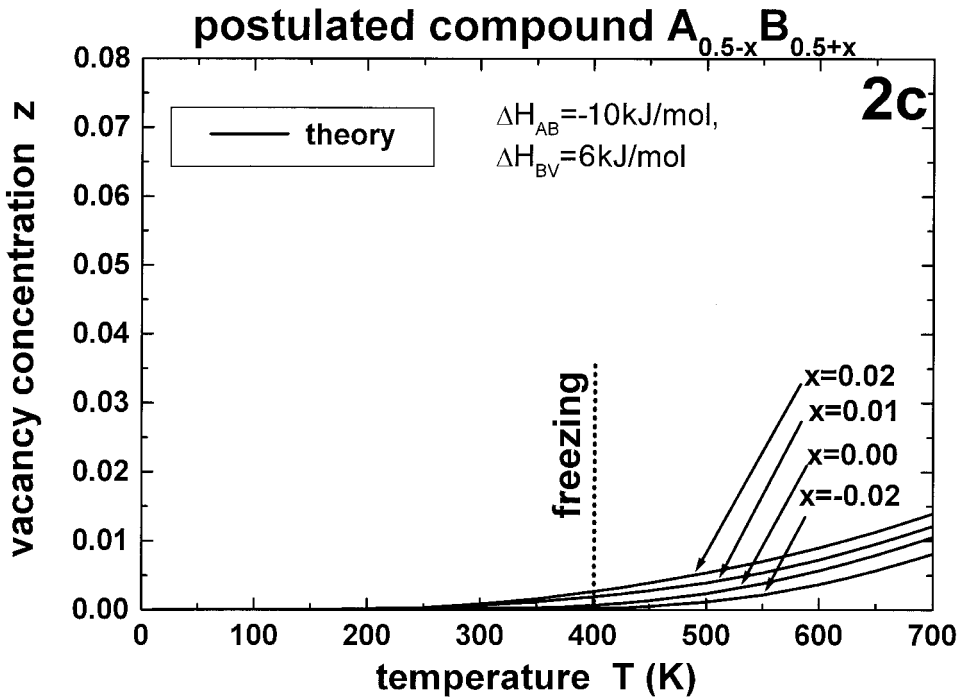
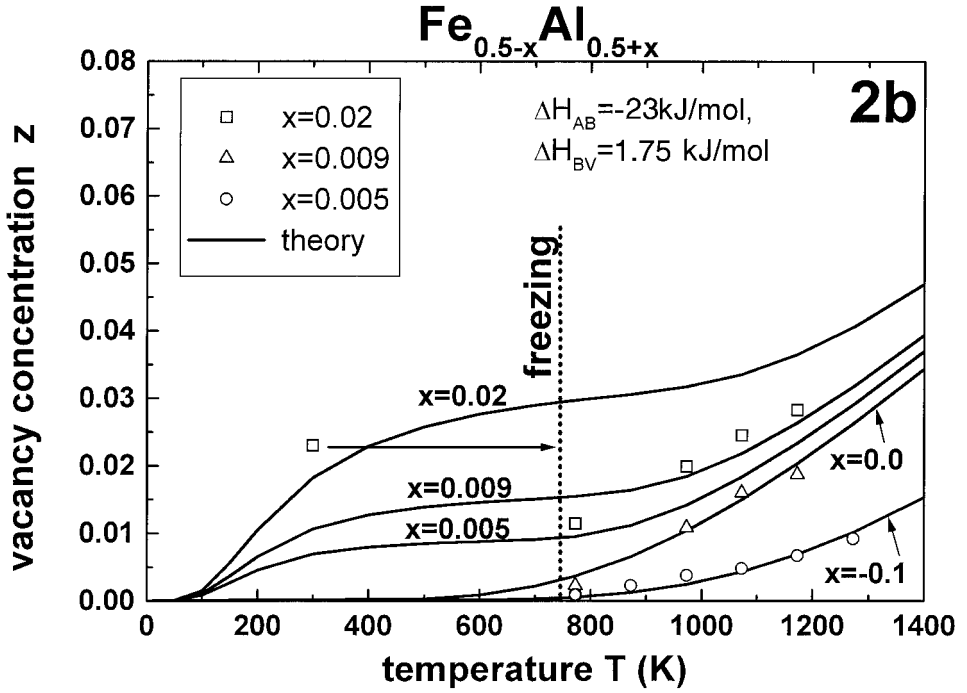


Figure 2. Continued.

are included in figure 2(a) and (b) for comparison, but no reliable quantitative experimental data in near-ASD type intermetallics (figure 2(c)) are available for a direct comparison.

From figures 2(a) and (b), we can see that the theoretical results are in good agreement with experimental data for near-TRD-type NiAl and hybrid-type FeAl. Our model reproduces the important and well known fact that strong B2 intermetallics tend to form a very high concentration of vacancies on one side of stoichiometry, and these high vacancy concentrations depend little on temperature above the diffusion freezing temperature. One should note that equilibrium defect concentrations cannot be realized below the freezing temperature; so it is not possible to compare with experiment at low temperatures. It also well reproduces the fact that hybrid intermetallics such as FeAl show a rather high concentration of vacancies on one side of stoichiometry; yet the vacancy concentration demonstrates an appreciable temperature dependence. Figure 2(c) gives a good qualitative explanation for the well known fact that vacancy concentrations of ASD (near-ASD)-type intermetallics exhibit a strong temperature dependence, but relatively weak composition dependence, and they contain a relatively lower vacancy concentration than the TRD-type and hybrid-type intermetallics.

We can draw an important conclusion from figure 2. *It is impossible to fit the temperature dependence of the vacancy concentration in intermetallics by a simple exponential function such as $z = A \exp(-E_f/RT)$* , in contrast with the case of all metals and disordered alloys. This conclusion is more evident in intermetallics containing a high vacancy concentrations such as the near-TRD type and the hybrid type. This is a natural result of our model, because our model shows that vacancy formation is due to the competition between ASD and vacancy formation; thus it is impossible to form vacancies alone without considering the competing ASD. Such competition cannot be expressed by a simple exponential function; instead, it is expressed by equations (4). Many previous studies tried to obtain the 'vacancy formation energy' in B2 intermetallics by making an exponential fit to the temperature dependence of the vacancy concentrations. Because of the above-mentioned problem, this 'vacancy formation energy' does not have a well defined physical meaning. The 'exponential fit', as widely performed, is merely an approximation of the high-temperature portion of the vacancy concentration curves shown in figure 2, which change greatly at low temperatures. Recently, Mayer and Fähnle (1997) also pointed out that the 'vacancy formation energy' obtained this way does not have a simple physical meaning.

§6. ANTISTRUCTURE DEFECT CONCENTRATIONS IN DIFFERENT TYPES OF B2 INTERMETALLICS AS A FUNCTION OF COMPOSITION AND TEMPERATURE

With the two energy parameters ΔH_{AB} and ΔH_{BV} determined in table 2, using equations (5b') and (1') (with approximations $z = z_\alpha$, and $z_\beta = 0$) we can calculate the A-ASD concentration y_A and B-ASD concentration y_B (here B-ASD represents the ASD species with large atomic sizes, e.g. Al and Cd, which are usually regarded as unlikely to form) as a function of the composition and the temperature for near-TRD-type NiAl, hybrid-type FeAl and a postulated near-ASD compound (behaving as figure 1(e)). The composition dependence of the A-ASD and B-ASD concentrations are shown in figures 3(a), (b) and (c) for three different types of B2 intermetallic. The corresponding temperature dependences of the B-ASD concentrations are shown in figure 4(a), (b) and (c) respectively.

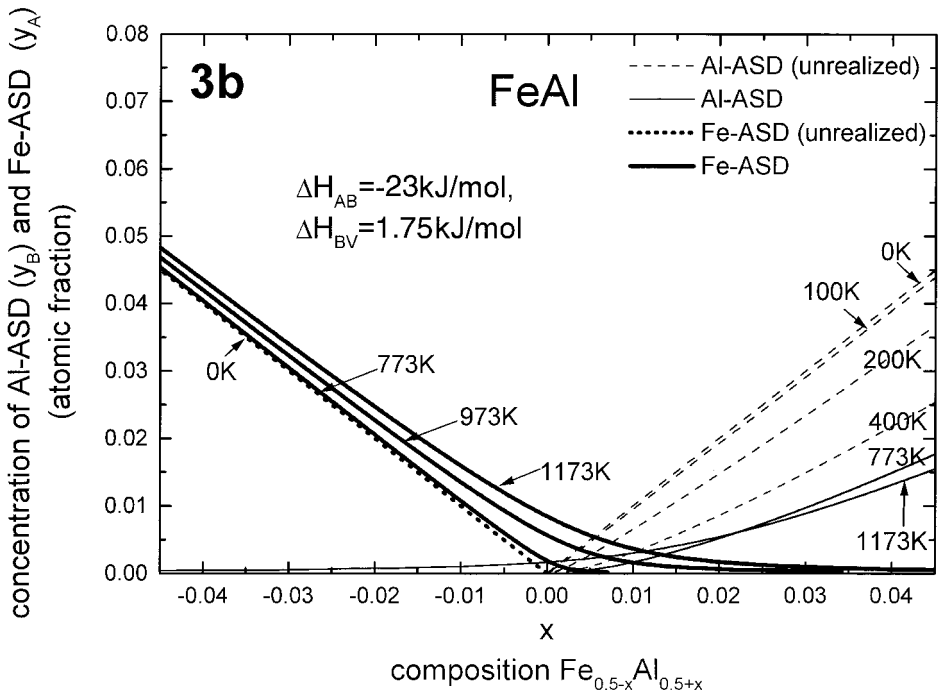
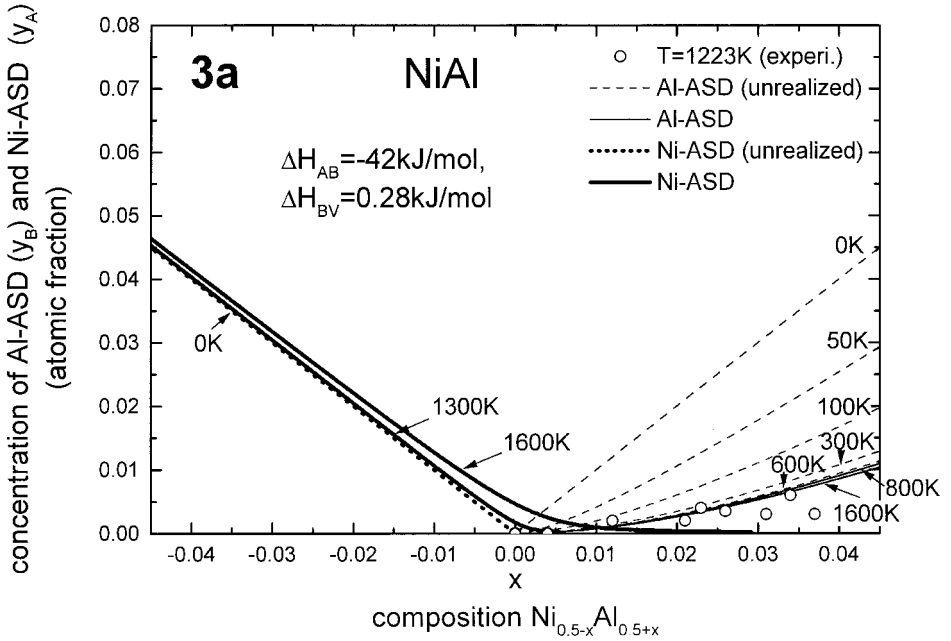
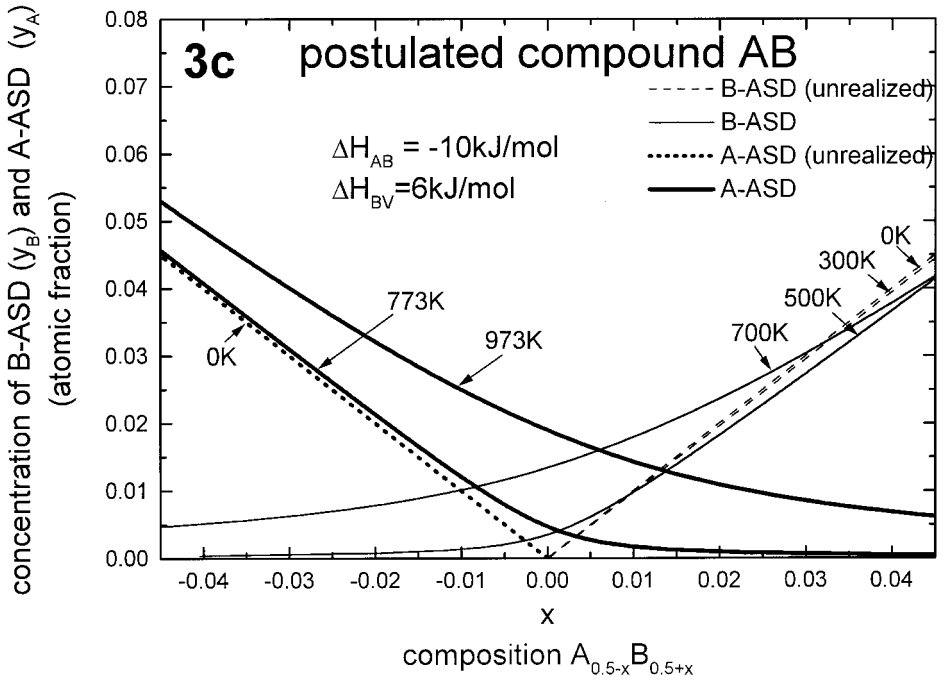


Figure 3. Composition dependences of the B-ASD and A-ASD concentrations for (a) near-TRD-type NiAl, (b) hybrid-type FeAl and (c) near-ASD-type AB (behaving as figure 1 (e)). Available data for NiAl (Kogachi *et al.* 1995) are included in (a) for comparison.



We can see that, for all different types of B2 intermetallic, there exist an appreciable amount of B-ASDs on the B-rich side of stoichiometry. Even the near-TRD compound NiAl, which has been assumed to contain no B-ASDs by the TRD model, contains an appreciable amount (0–1% depending on x) of such ASDs at any temperature. The calculated result for NiAl is in good agreement with the experimental data of Kogachi *et al.* (1995) obtained by measuring X-ray diffraction intensities (order parameters) (Kogachi *et al.* 1992). For hybrid-type and near-ASD-type intermetallics, the B-ASD concentrations are even higher (figures 3 (b) and (c) and figures 4 (b) and (c)). This is a natural consequence of the lower ordering energy of these compounds, because a lower ΔH_{AB} favours the formation of both A-ASDs and B-ASDs according to equation (4a).

From figure 4, we can see that the B-ASD concentration shows little temperature dependence (above the freezing temperature) for the near-TRD intermetallic NiAl, while for hybrid and near-ASD intermetallics the B-ASD concentration exhibits a rather strong temperature dependence. This difference also arises from the difference in the ordering energy, which determines the production of ASDs. The invariance of Al-ASD with temperature in the strong intermetallic compound NiAl (figure 4 (a)) is in good quantitative agreement with the experimental data of Kogachi *et al.* (1995).

§7. PREDICTIONS

Our model gives a clear physical picture for point-defect formation in B2 intermetallics by virtue of its simplicity and its clear relation to well defined energy parameters ΔH_{AB} , ΔH_{BV} and ΔH_{AV} , which characterize the given intermetallic compound. Based on such a model, we are able to make the following predictions.

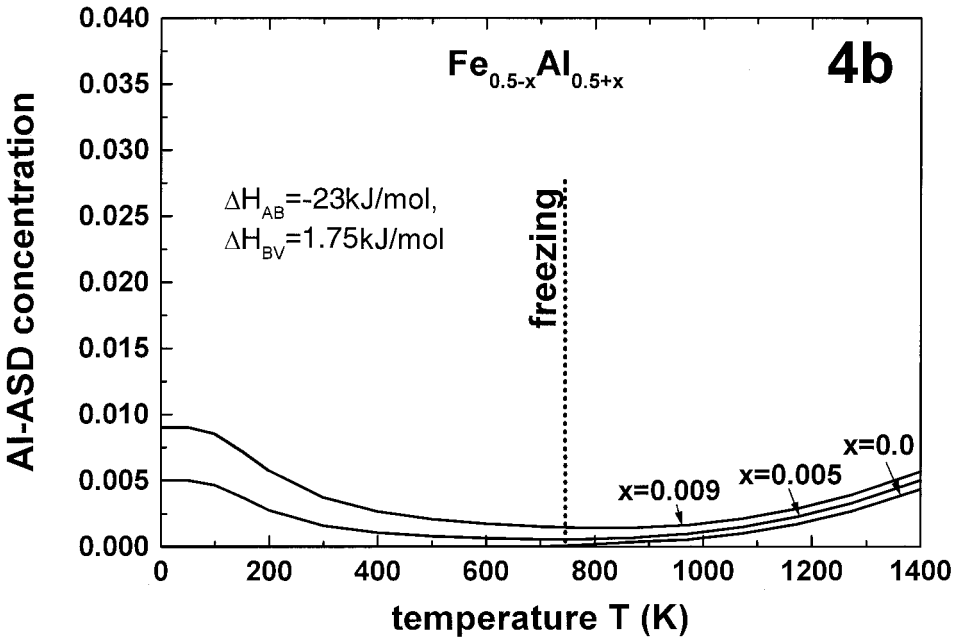
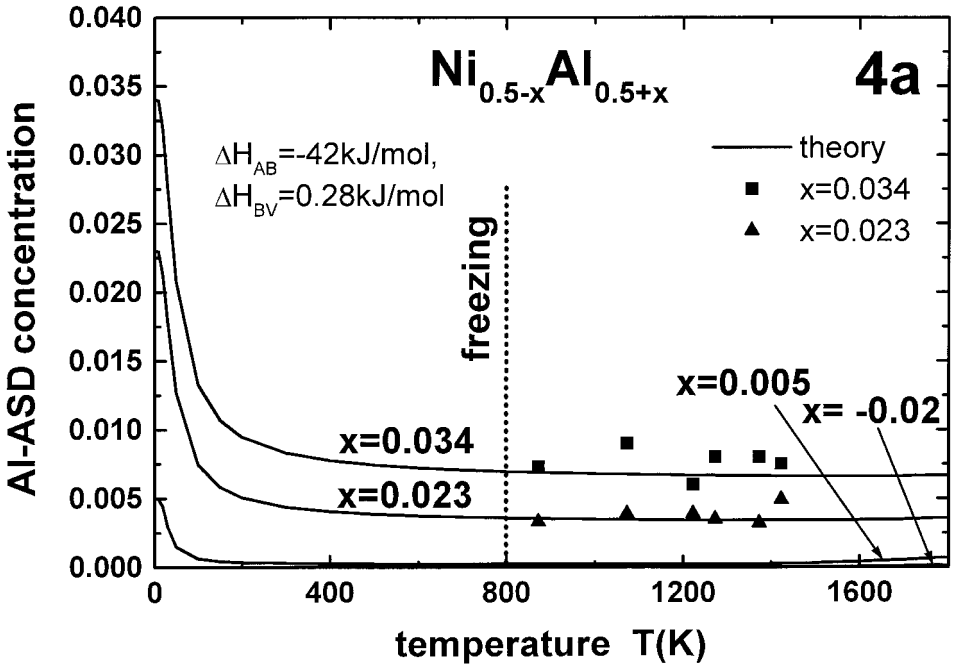
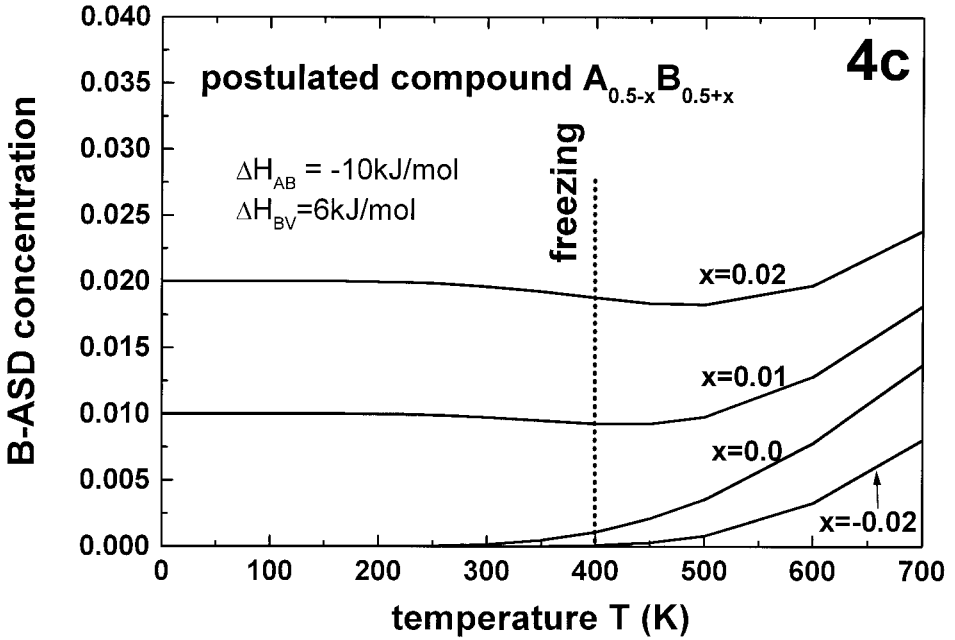


Figure 4. Temperature dependences of the B-ASD concentrations for (a) near-TRD-type NiAl, (b) hybrid-type FeAl and (c) near-ASD-type AB, which behaves as figure 1 (e). The data of Kogachi *et al.* (1995) for NiAl are included in (a) for comparison.



7.1. Vacancy concentration is asymmetrical about stoichiometry for all B2 intermetallics (expected to be true for intermetallics of other structures as well)

From equations (4), one can easily find that z_{α} and β are symmetrical about stoichiometry only when $\Delta H_{BV} = \Delta H_{AV}$, that is the two sublattices have the same tendencies to form vacancies. However, this condition can never be satisfied for intermetallics, because all intermetallics are characterized by a distinction between different sublattices. As discussed earlier, such a distinction makes the tendency of vacancy formation rather different in the two sublattices; thus there is always a great difference between ΔH_{BV} and ΔH_{AV} . As a consequence, vacancies tend to form predominantly in one sublattice that is characterized by a smaller vacancy-ASD barrier. We also anticipate that this feature holds for intermetallics of other structures, because the above-mentioned physical picture is independent of the structure of intermetallics. Owing to the non-equivalence of the vacancy formation in the two sublattices, the vacancy concentration does not exhibit symmetry about stoichiometry.

By using the master equations (4), we can calculate the relationship between the composition dependence of total vacancy concentration and the ratio m of ΔH_{AV} to ΔH_{BV} for a compound with $\Delta H_{AB} = -23 \text{ kJ mol}^{-1}$ at $T = 973 \text{ K}$ (i.e. taking the values of a hybrid-type FeAl). The result is shown in figure 5. We can easily see that the total vacancy concentration exhibits symmetry about stoichiometry only when $\Delta H_{BV} = \Delta H_{AV}$ (or $m = 1$), but this result obviously contradicts the experimental result shown in figure 1(c). In fact, such a symmetric dependence has never been reported in any B2 intermetallics, even including the weak AuCd. From figure 5, we find that the calculated result is in agreement with the experimental data (figure 1(c)) only when $\Delta H_{AV} \gg \Delta H_{BV}$, that is the formation of a vacancy in one sublattice (β sublattice) is much more difficult than in the other sublattice. Similar results can be obtained for near-TRD-type and near-ASD-type intermetallics. This is the reason why the simplified master equations (5) (which used this assumption) also give

excellent agreement with experimental results. For this reason, the total vacancy concentration shows a monotonic dependence on the composition parameter for all kinds of intermetallic, as can be seen in figure 1, although the composition dependence is weak for near-ASD intermetallics (figure 1 (e)).

Krachler *et al.* (1989) concluded from their model that the vacancy concentration in ASD-type (near-ASD in our terminology) intermetallics is symmetrical about stoichiometry. This is obviously different from the prediction of our model. The apparent asymmetry of vacancy concentrations for AuCd (figure 1 (d)), which was thought to be ‘ASD type’, is inconsistent with their conclusion, being consistent with our prediction. We anticipate that further precise vacancy measurement on near-ASD-type intermediates (e.g. AuZn and FeCo) can resolve the dispute.

In fact, we can simply prove that the simplified equations (5) correspond to $m = \infty$, that is the formation of a vacancy in one sublattice (β) is completely forbidden. We can see from figure 5 that, if the difference between ΔH_{BV} and ΔH_{AV} is not large enough, a small amount of B vacancies can be produced on the A-rich side; thus the total vacancy concentration on the A-rich side of stoichiometry is slightly higher than that predicted by equations (5), and the total vacancy concentration on the B-rich side of stoichiometry is slightly lower than predicted by the simplified equations. Unfortunately, the experimental uncertainty in vacancy measurement usually exceeds such a small difference; thus we are not able to give a more accurate description of the defect structures for intermetallics using equations (4). Thus equations (5) may be accurate enough for most cases. For near-ASD compounds, it is

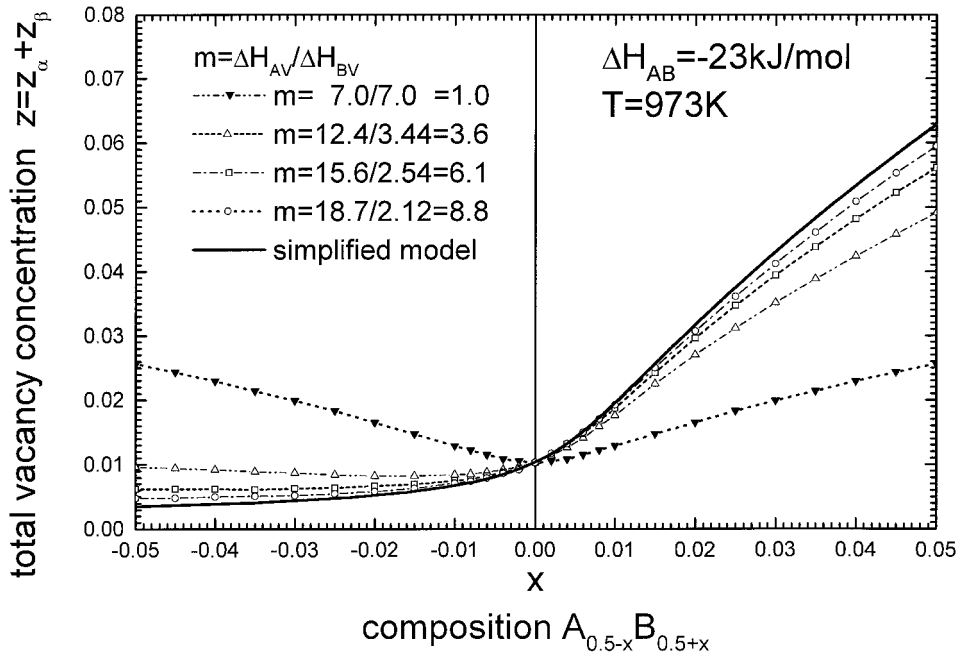


Figure 5. Influence of the ratio $m = \Delta H_{AV}/\Delta H_{BV}$ on the composition dependence of the total vacancy concentration $z (= z_{\alpha} + z_{\beta})$ for the B2 intermetallic compound with $\Delta H_{AB} = -23 \text{ kJ mol}^{-1}$ at $T = 973 \text{ K}$. The simplified model corresponds to $m = \infty$. In order to make comparison possible, experimentally determined $z = 0.01$ at stoichiometry ($x = 0$) is imposed on calculations using different m values.

likely that m is not very large. In this case, the use of equation (4) may be preferred. Unfortunately, to date we have no reliable quantitative vacancy data for near-ASD-type intermetallics (except for AuCd shown in figure 1 (*d*), which was thought to belong to the ASD type) to compare with our model. We anticipate that much experimental work will be done in future on such compounds.

7.2. Near-antistructure-defect-type B2 intermetallic compounds may contain quite a high amount of vacancies (e.g. 0.5–1%) at high temperatures

This type of B2 intermetallic has commonly been considered to be similar to disordered alloys or pure metals which contain a negligible amount of vacancies (less than 0.1%) even at the melting temperature. As discussed above, intermetallics are completely different from the single-lattice crystals in point-defect formation, and the vacancy concentration is determined by the competition between vacancy formation and ASD formation. Although vacancy formation is unfavourable at low temperatures owing to the internal energy consideration (ASD is the ground state), at high temperatures vacancies may become favourable owing to its higher contribution to entropy (vacancy accommodation yields a vacancy concentration twice the ASD concentration for ASD accommodation). Thus vacancies become favourable at high temperatures, and the amount of vacancies is determined by the energy barrier ΔH_{BV} . Here we note from table 2 that, for all B2 intermetallics, the energy barrier is low (less than a few kilojoules per mole), and even lower for near-TRD- and hybrid-type intermetallics. This is a feature of all B2 intermetallics, and it can be understood from the open feature of the B2 structure. An open structure has fewer nearest-neighbour atoms than a close-packed structure such as $L1_0$; thus the formation of a vacancy breaks fewer AB bonds which are favourable in intermetallics and thus has less energy disadvantage compared with close-packed intermetallics. This is the reason why open B2 intermetallics exhibit a high vacancy concentration while close-packed intermetallics such as $L1_0$, $L1_1$ and $D0_{22}$ contain, very few vacancies even at high temperatures. A similar consideration has also been proposed by Badura and Schaefer (1993).

The open B2 structure makes vacancy formation easy even in near-ASD-type B2 intermetallics, and at high temperatures the concentration may reach quite a remarkable value such as 0.5–1%, as shown in figure 1 (*e*) and figure 2 (*c*). Because the vacancy concentration is rather high around the diffusion freezing temperature (see figure 2), an appreciable amount of vacancies (e.g. 0.1–0.5%) may be frozen down to low temperatures. Under careful experimental conditions; vacancy measurement by a combination of lattice parameter determination and macroscopic density measurement may yield an acceptable accuracy (e.g. 0.2%) to test this prediction. Thus it is possible to verify the above prediction by such an experiment on near-ASD-type intermetallics (e.g. AuZn and FeCo). Positron annihilation experiments are not able to give a quantitative vacancy concentration at such a high concentration.

The above prediction may shed new light on many important problems, such as diffusion in B2 intermetallics (Koiwa 1992, Nakajima *et al.* 1996), and the role of point defects in the diffusionless martensitic transformation of some B2 intermetallics (e.g. TiNi, AuCd and CuZnAl) which determines the technologically important shape memory effect (Ren *et al.* 1999b), and the role of point defects on ageing phenomena in shape memory alloys (Ren and Otsuka 1997). Many previous investigations of these problems followed the common assumption that the

vacancy concentration in these intermetallics is less than 0.1% even at high temperatures. The alteration of this postulation may bring about new insight into these important issues.

§8. RESTRICTIONS OF THE PRESENT MODEL

Before concluding this paper, we would like to point out the restrictions of our model due to the assumption that defect concentrations are much less than unity. This assumption is expected to be obeyed in the whole temperature range of near-TRD intermetallics and hybrid intermetallics because these intermetallics remain well ordered up to melting temperature (i.e. the ASD concentration is not high). However, for weak intermetallics such as near-ASD type, the order-disorder transition may occur prior to melting, and thus this assumption becomes invalid near T_c because the ASD concentration may be very high at such temperatures. Therefore, for near-ASD-type intermetallics our model is expected to be valid at not too high temperatures (e.g. $T < 0.7T_c$). Although our model cannot give a quantitative evaluation of the vacancy concentrations around T_c , we expect that there is a drop in vacancy concentration around T_c prior to disordering, because disordered alloys do not contain a high concentration of vacancies. The vacancy concentration is expected to show an increase again when the temperature is higher than T_c , as a result of the common thermal effect. Also, vacancies may occupy both sublattices in a comparable amount near T_c , because the two sublattices become less distinguishable near T_c .

§9. CONCLUSIONS

We proposed a unified model which is able to describe both the composition dependence and the temperature dependence of the point-defect concentration in B2 intermetallics. This model, in a simple mathematical form, clearly manifests the fundamental principle of point-defect formation in B2 intermetallics (which may be common for all intermetallics). Point-defect formation in intermetallics is different from that in single-lattice crystals, it is controlled by the competition between two entropy production processes: vacancy formation or ASD formation in the two sublattices. The calculated composition and temperature dependences of the vacancy concentration from the present model are in excellent agreement with experimental results for different types of B2 intermetallic i.e. near-TRD type, hybrid type and near-ASD type. Based on the present study, we conclude that no constitutional vacancies exist in all B2 intermetallics, and they are also unlikely in other intermetallics. As a consequence, there exists no fundamental difference between the three different types of B2 intermetallic, all of which can be satisfactorily described by the present model. We show that there is a significant difference in the ease of vacancy formation in the two sublattices for all B2 intermetallics, and consequently vacancies form predominantly in one sublattice. This leads to a prediction that the vacancy concentration is not symmetrical about stoichiometry for all B2 intermetallics. Based on the ease of vacancy formation in the open B2 structure, we further predict that the vacancy concentration may be quite high (0.5–1%) at elevated temperatures even in near-ASD-type intermetallics.

ACKNOWLEDGEMENTS

We thank Professor M. Kogachi of the University of Osaka Prefecture for enlightening discussions. We also thank Professor R. W. Cahn, FRS, of the

University of Cambridge for kindly reading the manuscript and for stimulating discussions. This work was supported by Grant-in-Aid for Research on Priority Area of Phase Transformations (1997–1999) and partially supported by Grant-in-Aid for Scientific Research (X. R. Syorei) from the Ministry of Education, Science and Culture of Japan.

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