

# Effect of interaction energies on the vacancy behaviour in B2 ordered intermetallics

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## Abstract

We examine the correlation between the interaction energies used in a nearest neighbour mean field model and  $x_v$ , the vacancy concentration, in B2 intermetallic alloys. The range of vacancy behaviour has been classified into four generic categories. In particular, a condition on interaction energies is derived for the alloys to exhibit constitutional vacancies (Type III behaviour in our classification). The existing theoretical results for NiAl, FeAl, CoAl, NiGa, CoGa and AuCd have been analysed within the framework of our classification scheme, and rationalized using the interaction energies used in those studies. Since different sets of interaction energies may predict the same vacancy behaviour, we conclude that experimental verification should not only use measurements of  $x_v$ , but also the measurement of other point defects. An examination of the relative atomic size of B in comparison with the nearest neighbour distance in the B2 structure reveals that it could be an important reason for the aluminides to exhibit constitutional vacancies. However, this size effect is not a significant factor in NiGa, CoGa and AuCd. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Point defects in intermetallics have been studied extensively (see [1] for a review). They are interesting from a fundamental viewpoint because the various sublattices in intermetallics are not equivalent, and hence defects in intermetallics may show special features. In particular, the B2 ordered intermetallics have been studied in great detail for their defect properties (see [2] for a detailed review).

Of the many theoretical studies [2–13], quite a few have applied a Bragg–Williams type mean field theory (which is well known in the literature, see for example [14]), to a model in which the interatomic interactions are assumed to be through pairwise bonds. Though the interactions may extend to higher neighbour shells [7], they are typically assumed to be only between the nearest neighbours, as in the present work. However, neither the interaction energies used as inputs into these

models nor the predictions based on these models for various intermetallics studied viz., NiAl, FeAl, CoAl, CoGa, NiGa and AuCd, agree among themselves. Since the underlying model is the same, the differences in the predictions could only be due to the different interaction energies used. Hence, our main aims in this paper are

- to rationalise the findings of the various mean field studies based on the interaction energies that are used in those studies; and
- to critically assess both the interaction energies, and the results based on those interaction energies.

With these aims in mind, we first study the effect of interaction energies on the vacancy behaviour in B2 ordered intermetallics, treating the former as generic parameters. We systematically vary the interaction energies, and determine the range of behaviour that arise as a result. Using this procedure, we also identify the conditions under which the Bradley–Taylor behaviour (wherein the B-rich alloys exhibit constitutional vacancies) is obtained. The correlation between interaction energies and vacancy behaviour thus established is then used to provide a perspective on the diverse mean field results on NiAl, FeAl, CoAl, CoGa, NiGa and AuCd.

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Further, we have also examined how well the atomic size effect is able to explain the Type II or Type III behaviour (which are described in Section 3.1) in these B2 alloys. We show that while such an explanation is satisfactory for aluminides, it is inadequate for NiGa, CoGa and AuCd.

This paper is organised as follows. The next section presents the salient features of the nearest neighbour model, and the mean field formulation used for determining the concentrations of various point defects. Section 3 describes and discusses our results on the correlation between interaction energies and vacancies with specific reference to the existing mean field studies and the effect of relative atomic size of B (in B2 and pure B crystal structures) on the Type II or Type III behaviour. We end the paper with a summary of our conclusions.

## 2. Mean field formulation

A brief outline of the mean field formulation is as follows (for more details, see [7,15]): We consider a rigid, body centred cubic (bcc) lattice divided into two interpenetrating simple cubic lattices referred to as  $\alpha$  and  $\beta$  sublattices, consisting of cube corners and body centers, respectively. Let  $N$  be the total number of lattice sites. If  $N_X$  is the number of  $X$  species ( $X = A, B$  or  $V$ ) and if  $N_\theta$  is the number of  $\theta$  sublattice sites ( $\theta = \alpha$  or  $\beta$ ),

$$N = N_\alpha + N_\beta = N_A + N_B + N_V = N_{\text{mol}} + N_V, \quad (1)$$

where  $N_{\text{mol}}$  is the Avogadro number. Assuming only the nearest neighbour interactions to exist, a mean field expression is written for the internal energy ( $E$ ) and the entropy ( $S$ ) in the Bragg–Williams approximation as follows:

$$E = \frac{Nz}{2} [x_A^\alpha x_A^\beta e_{AA} + x_B^\alpha x_B^\beta e_{BB} + x_V^\alpha x_V^\beta e_{VV} + (x_A^\alpha x_B^\beta + x_B^\alpha x_A^\beta) e_{AB} + (x_A^\alpha x_V^\beta + x_V^\alpha x_A^\beta) e_{AV} + (x_B^\alpha x_V^\beta + x_V^\alpha x_B^\beta) e_{BV}], \quad (2)$$

$$S = -\frac{k_B N}{2} [x_A^\alpha \ln x_A^\alpha + x_A^\beta \ln x_A^\beta + x_B^\alpha \ln x_B^\alpha + x_B^\beta \ln x_B^\beta + x_V^\alpha \ln x_V^\alpha + x_V^\beta \ln x_V^\beta], \quad (3)$$

where,  $x_X^\theta = N_{X\theta}/N_\theta$  ( $N_{X\theta}$  is the number of species  $X$  occupying  $\theta$  sublattice),  $e_{XY}$  is the  $XY$  interaction energy ( $X, Y = A, B$  or  $V$ ),  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $z$  is the number of nearest neighbours. The free energy  $G$ , at any temperature is given by

$$G = E - TS. \quad (4)$$

Using the constraint that the number of  $\alpha$  sublattice sites is equal to that of the  $\beta$  sublattice sites, and by defining three auxiliary parameters  $\eta_1$ ,  $\eta_2$  and  $\eta_3$  as in Eqs. (5)–(7) below, the free energy can be written in terms of the alloy composition  $x_B$ , temperature  $T$ , interaction energies  $e_{XY}$ , and the auxiliary parameters  $\eta_1$ ,  $\eta_2$  and  $\eta_3$  only. The auxiliary parameters are defined as follows:

$$\eta_1 = \frac{N_V}{N_{\text{mol}}}, \quad (5)$$

$$\eta_2 = \frac{2(N_{B\beta} - N_{B\alpha})}{N_{\text{mol}}}, \quad (6)$$

and

$$\eta_3 = \frac{2(N_{V\beta} - N_{V\alpha})}{N_{\text{mol}}}. \quad (7)$$

Here,  $\eta_1$  refers to the vacancy concentration, while  $\eta_2$  and  $\eta_3$  refer to the normalised, differential B atom and vacancy population, respectively, over the two sublattices. Now, knowing the interaction energies  $e_{XY}$ , for a given  $x_B$  and  $T$ , the free energy expression Eq. (4) can be minimized with respect to the three auxiliary parameters. From such a minimization, we can obtain

1. the vacancy concentration for a given  $x_B$  and  $T$ ;
2. the differential B atom and vacancy concentration on the  $\alpha$  and  $\beta$  sublattices for a given  $x_B$  and  $T$ ;
3. the free energy as a function only of  $x_B$  and  $T$ .

## 3. Results and discussion

### 3.1. Range of vacancy behaviours

The existing mean field studies on various B2 intermetallics use diverse values of interaction energies (see Table 3). Such diverse values of interaction energies could lead to

- different predictions, as in the case of NiAl, where Kim [9] predicts Type III behaviour while others [10–12] do not (see below), or
- to the same prediction, as in the case of FeAl, where all the studies [13,10–12] predict Type II behaviour (see below).

The formalism in all these studies are the same, and as described in Section 2, the only difference between the various studies is the interaction energy values used by them. Our aim is to rationalise the various results reported by these various mean field studies on various intermetallics with reference to the interaction energies used in them. In order to facilitate the rationalisation, we study the vacancy behaviour of B2 intermetallics by systematically varying the interaction energies. The range of behaviour thus obtained by varying the interaction energies may roughly be classified into four types

Table 1  
Interaction energies used in the calculation (in eV)

System label	$e_{AA}$	$e_{BB}$	$e_{AB}$	$e_{AV}$	$e_{BV}$	$V_{AB}$	$V_{AV}$	$V_{BV}$
$A_1$	-0.4	-0.35	-0.515	0.0	0.0	-0.28	0.4	0.35
$A_2$	-0.4	0.0	-0.34	0.0	0.0	-0.28	0.4	0.0
$A_3$	-0.4	0.11	-0.285	0.0	0.0	-0.28	0.4	-0.11
$A_4$	-0.4	0.24	-0.22	0.0	0.0	-0.28	0.4	-0.24
$B_1$	-0.4	-0.35	-0.515	-0.08	-0.07	-0.28	0.24	0.21
$B_2$	-0.4	0.0	-0.34	-0.08	0.00	-0.28	0.24	0.0
$B_3$	-0.4	0.11	-0.285	-0.08	0.022	-0.28	0.24	-0.066
$B_4$	-0.4	0.36	-0.16	-0.08	0.072	-0.28	0.24	-0.216
$C_3$	-0.4	-0.1	-0.4	-0.04	-0.08	-0.3	0.32	-0.06

viz., Type I, Type II, Type III and Type IV. Here, we briefly describe these four types of behaviour. A detailed discussion of the same could be found elsewhere [8].

- Type I: The vacancy concentration is uniformly low throughout the entire composition range.
- Type II: The vacancy concentration is low in A-rich and stoichiometric alloys. In the B-rich alloys, the vacancy concentration is comparatively high (several percent) and increases with increasing  $x_B$ . However, the vacancy concentration is less than  $2\delta$  where  $\delta$  is the deviation from stoichiometry.
- Type III: The vacancy concentration is low in A-rich and stoichiometric alloys. However, the B-rich alloys obey the Bradley–Taylor condition for constitutional vacancies:  $x_v = 2\delta$ . In this case, all the off-stoichiometry  $\delta$  in B-rich alloys is accommodated by creation of an appropriate number ( $2\delta$ ) of vacancies in the  $\alpha$  sublattice.
- Type IV: The vacancy concentration is uniformly high throughout the composition range studied.

A few of the existing mean field studies assume that the  $e_{AV}$  and  $e_{BV}$  energies are zero while others do not. Keeping this in mind, here, we have calculated the point defect concentrations for different systems. All these systems are listed in Table 1: for all the systems, we have assumed only the nearest neighbour interactions; in addition, we have assumed that  $e_{VV} = 0$ , and  $e_{AA} = -0.4$  eV. The first four systems (labelled  $A_1$ – $A_4$ ) assume the  $e_{AV}$  and  $e_{BV}$  energies to be zero and  $e_{BB}$  is systematically varied while keeping the order–disorder transformation temperature,  $T_c$ , at about 6500 K for the stoichiometric alloy with no vacancies ( $T_c = 2V_{AB}/k_B$ , where  $V_{AB} = 2e_{AB} - e_{AA} - e_{BB}$ ). The next four systems (labelled  $B_1$ – $B_4$ ) assume non-zero values for  $e_{AV}$  and  $e_{BV}$  (20% of  $e_{AA}$  and  $e_{BB}$ , respectively) and  $e_{BB}$  is again systematically varied while keeping  $T_c$  a constant as before. The system labelled  $C_3$  is chosen with the specific purpose of showing that Type III behaviour is possible even when  $e_{BB}$  is attractive.

In Fig. 1, the variation of  $x_v (= N_v/N_{mol})$ , the vacancy concentration, with  $x_B$ , the alloy composition, at 1000 K is shown for systems  $A_1$ – $A_4$ ; the behaviour of  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  correspond to Type I, Type II, Type III and Type IV, respectively.

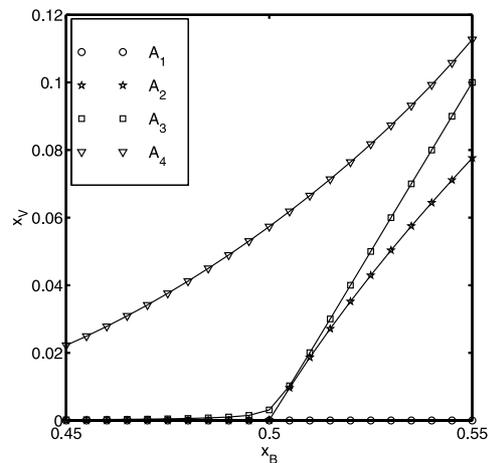


Fig. 1. Dependence of the vacancy concentration ( $x_v$ ) in alloy composition for systems  $A_1$ – $A_4$  ( $T = 1000$  K).

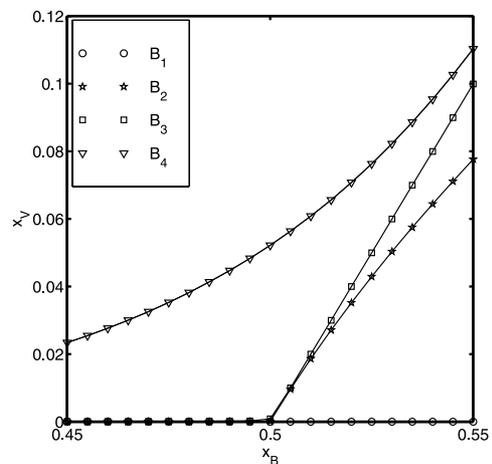


Fig. 2. Dependence of the vacancy concentration ( $x_v$ ) in alloy composition for systems  $B_1$ – $B_4$  ( $T = 1000$  K).

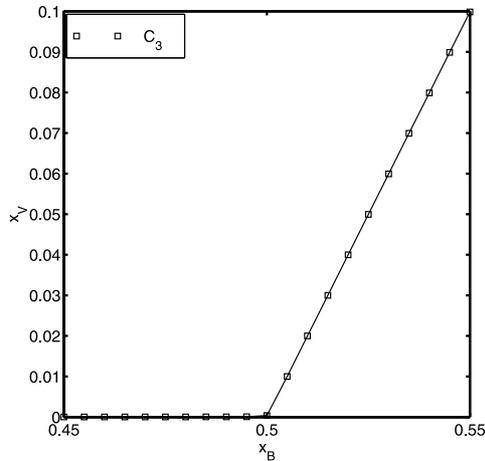


Fig. 3. Dependence of the vacancy concentration ( $x_v$ ) in alloy composition for system  $C_3$  ( $T = 1000$  K).

In Fig. 2, we present the variation of  $x_v$  with  $x_B$  at 1000 K for systems  $B_1$ – $B_4$ . It is clear from this figure that, even with finite values for  $e_{AV}$  and  $e_{BV}$ , it is possible to obtain the four types of vacancy behaviour seen in Fig. 1.

In Fig. 3, we show that the  $x_v$  versus  $x_B$  curve for  $C_3$  (which assumes the  $e_{BB}$  energy to be negative) belongs to Type III.

For the Type III behaviour obtained for the systems  $A_3$ ,  $B_3$  and  $C_3$  to be truly equivalent to the classical Bradley–Taylor behaviour, the vacancy concentration in the B-rich alloys must also be independent of temperature. Our calculations for a 52.5% B alloy up to 1500 K does indicate that  $x_v$  is indeed independent of temperature.

Although the systems  $A_3$ ,  $B_3$  and  $C_3$  lead essentially to the same behaviour for  $x_v$ , they do yield significantly different results for sublattice populations of vacancies and atoms, and their temperature dependence. Thus, it is incorrect to predicate the ‘success’ of any theory only on experiments on  $x_v$ ; the theory should be validated against experimental results on other quantities, including antisite defects. This is discussed in detail below.

### 3.2. Constitutional vacancies: condition on interaction energies

Kim [9,13] showed that, for constitutional vacancies (Type III behaviour) to be observed in B-rich alloys, B–B interactions must be repulsive under the condition that  $e_{AV} = e_{BV} = 0$ . When the vacancy–atom interaction has a finite energy, it is possible to get constitutional vacancies even when  $e_{BB} < 0$ , as shown below.

A condition on the interaction energies for obtaining Type III behaviour is obtained by the following consideration: In the stoichiometric alloy, triple defects would

predominate over antisite defects if the former have a lower formation energy than the latter. If the formation energy of a vacancy on the  $\alpha$  sublattice is  $E_{V,\alpha}^f$  and if the formation energy of an antisite on the  $\alpha$  sublattice is  $E_{anti,\alpha}^f$ , the above condition can be shown to be equivalent to the following:

$$2E_{V,\alpha}^f - E_{anti,\alpha}^f < 0. \quad (8)$$

Assuming only the nearest neighbour interactions to exist in the system, and using a simple bond breaking model, it can be shown that Eq. (8) implies the following equation (see the appendix in [7,15]).

$$V_{BV} = 2e_{BV} - e_{BB} < 0. \quad (9)$$

Within the framework of this model, the existence of triple defects in the stoichiometric alloy implies the existence of constitutional vacancies in B-rich alloys. Thus, the constitutional vacancy behaviour will be exhibited for a wide range of interaction parameters as long as Eq. (9) is obeyed. In particular, if  $e_{BV}$  and  $e_{AV}$  are considered to be zero, then the triple defect behaviour will be exhibited only for those alloys for which  $e_{BB}$  is positive (or, in other words, repulsive), a condition noted in [9,13].

### 3.3. A note on Type III behaviour

As discussed above, whenever Eq. (9) is obeyed, one would expect Type III behaviour. For Type III behaviour to be a true Bradley–Taylor behaviour, the vacancy concentration should also be independent of temperature. However, if Eq. (9) is not obeyed, the only conclusion that we can draw is that the alloy will not exhibit Type III behaviour and the actual behaviour depends on the other three interaction energies viz.,  $e_{AA}$ ,  $e_{AV}$  and  $e_{AB}$  which are not involved in Eq. (9).

Our analysis of the existing mean field studies also indicates that the temperature at which the calculations (or experiments) are carried out can have a profound influence on the results obtained. To be more specific, if the temperature at which calculations are carried out is more than  $0.2 T_c$ , where  $T_c$  is the order–disorder temperature in the defect-free, stoichiometric crystal, then there is a strong thermal contribution to the defect concentration as shown in Table 2 and discussed in the subsections on FeAl, CoGa and NiGa. Hence, it is essential that both experiments and calculations be carried out at temperatures below  $0.2 T_c$  to decide the type of vacancy behaviour exhibited.

### 3.4. Comparison with existing studies

Of the many existing theories of defects in B2 ordered intermetallics, we have specifically chosen the theories of Kim [9,13], Kogachi and Haraguchi [10], Ren and Otsuka [11] and Ren et al. [12], for our

Table 2  
Effect of temperature on the defect behaviour

System	Composition	Temperature (in $T_c$ )	$x_v$	Reference
FeAl	Fe-rich alloys	0.2	Very low	[10]
FeAl	Fe-rich alloys	0.26	0.2%	[11,12]
FeAl	Fe-rich alloys	0.4	0.6%	[11,12]
CoAl	Co-rich alloys	0.19	Very low	[11,12]
CoAl	Co-rich alloys	0.3	0.2%	[11,12]
CoAl	Co-rich alloys	0.38	0.7%	[11,12]
AuCd	Au-rich alloys	0.19	Very low	[11,12]
AuCd	Au-rich alloys	0.45	0.7%	[11,12]

discussion; these studies use nearest neighbour interactions, and hence can directly be compared with the present work. In Table 3, we list the effective interaction energies used in these studies, the fitting exercise undertaken to obtain these interaction energies, the reported vacancy behaviour, our predictions based on the reported interaction energies and the order–disorder temperature in the defect free, stoichiometric alloy corresponding to the  $V_{AB}$  values reported. However, since the interaction energies used in these various studies were obtained by fitting to the vacancy concentration data and later their predictions are compared with experimental results on the very quantity used for fitting, these diverse results, in our view, are only of limited validity.

Further, as we noted in Section 3.2, the temperature dependence and the sublattice occupancy of the vacancies and the atomic species will be different corresponding to the different interaction parameters used. But

there is a dearth of high-accuracy measurements of antisite and vacancy concentration in the stoichiometric and A-rich alloys. So, it is our belief that experiments aimed at obtaining these quantities will be of great use in validating the theoretical predictions. At the present stage, in the absence of any such experimental validation, none of the mean field theories listed in Table 3 could be pronounced to be ‘correct’ or ‘incorrect’ conclusively. Keeping these limitations in mind, we discuss below individually the various systems listed in Table 3.

### 3.4.1. NiAl

Based on the  $V_{BV}$  values used by Kim [9], we expect from Eq. (9), a Type III behaviour; on the other hand,  $V_{BV}$  values of Kogachi and Haraguchi [10], Ren et al., and Ren and Otsuka [11,12] lead us to predict a non-Type III behaviour. This is confirmed by Fig. 2(a) in [9] which shows Type III behaviour and by Fig. 5 in [10] and Fig. 1(a) in [11,12] where Type II behaviour is reported.

We also note that the vacancy concentration obtained by Ren et al., and Ren and Otsuka are more closer to the BT line (the  $x_v = 2\delta$  line) than those reported by Kogachi and Haraguchi in the Al-rich alloys.

### 3.4.2. FeAl

The  $V_{BV}$  value used by Kim is positive and so, based on Eq. (9) we can expect FeAl not to show Type III behaviour. This is confirmed by Fig. 2(a) in [13] which shows a behaviour which is similar to that of Type IV behaviour in our Fig. 1. We note, however, that under the column ‘Reported Behaviour’ in Table 3, we have listed Kim’s results to be of Type II. This is because the  $V_{AB}$  values used by Kim [13] corresponds to an order–disorder temperature of  $\sim 1996$  K in the defect free, stoichiometric alloy. Kim had carried out the defect concentration calculations at 1173 K. This value of the

Table 3  
Analysis of the interaction energies (in eV) used in the literature

System	Reference	$V_{AB}$	$V_{AV}$	$V_{BV}$	Fitting	Predicted behaviour	Reported behaviour	$T_c$ in K
NiAl	[9]	−0.344	0.3	−0.1	$x_v$	Type III	Type III	7984
	[10]	−0.360	0.147	0.013	$H_f$ and $x_v$	Not Type III	Type II	8356
	[11,12]	−0.218	N.A. <sup>a</sup>	0.001	$x_v$	Not Type III	Type II	5060
FeAl	[13]	−0.086	0.24	0.02	$x_v$	Not Type III	Type II <sup>b</sup>	1996
	[10]	−0.196	0.098	0.033	$H_f$ and $x_v$	Not Type III	Type II	4549
	[11,12]	−0.119	N.A. <sup>a</sup>	0.009	$x_v$	Not Type III	Type II	2762
CoAl	[11,12]	−0.181	N.A. <sup>a</sup>	0.005	$x_v$	Not Type III	Type II	4201
CoGa	[13]	−0.08	0.266	0.033	$x_v$	Not Type III	Type II <sup>c</sup>	1857
NiGa	[9]	−0.192	0.3	−0.1	$x_v$	Type III	Type III <sup>d</sup>	4456
AuCd	[11,12]	−0.066	N.A. <sup>a</sup>	0.016	$x_v$	Not Type III	Type II	1532

<sup>a</sup> N.A., not available.

<sup>b</sup> See the subsection on Section 3.4.2 for a detailed discussion.

<sup>c</sup> See the subsection on Section 3.4.4 for a detailed discussion.

<sup>d</sup> See the subsection on Section 3.4.5 for a detailed discussion.

Table 4  
Nearest neighbour distances in B2 intermetallics and pure metals

System	$D_1$ (in Å)	$D_G$ (in Å)	$R = (D_G - D_1)/D_1$
NiAl	2.49	2.86	0.15
FeAl	2.51	2.86	0.14
CoAl	2.47	2.86	0.16
CoGa	2.48	2.70	0.09
NiGa	2.49	2.70	0.08
AuCd	2.88	3.04	0.06

Note: The lattice parameter values for all the B2 alloys as well as the Goldschmidt radii in the native crystal structures of the B atoms were taken from Ref. [17].

temperature corresponds to  $\sim 0.6 T_c$  and hence there is a strong thermal contribution to the vacancy concentrations. Calculations carried out at 400 K (which corresponds to  $\sim 0.2 T_c$ ) using the interaction energies reported by Kim indicates that his model of FeAl belongs to Type II.

The  $V_{BV}$  values used by Kogachi and Haraguchi, Ren et al., and Ren and Otsuka are positive. So, we do not expect Type III behaviour to be predicted and this is confirmed by Fig. 8 in [10] and Fig. 1(c) in [11,12], where Type II behaviour is reported.

In this system also, the vacancy concentration obtained by Ren et al., and Ren and Otsuka are closer to the BT line than those reported by Kogachi and Haraguchi in Al-rich alloys. The vacancy concentration obtained by Kim lies above the BT line due to the predominant thermal contribution to the defect concentration as explained above.

The interaction energies used by all the studies [13,11,12,10] on FeAl are unrealistic. The phase diagram [16] of FeAl indicates that the stoichiometric FeAl disorders at 1583 K which fixes the bound on  $V_{AB}$  at  $-0.068$  while these studies use values within the range  $-0.086$  to  $-0.196$ .

### 3.4.3. CoAl

The  $V_{BV}$  values used by Ren et al., and Otsuka are positive. Hence, we do not expect Type III behaviour to be predicted and this is confirmed by Fig. 1(b) in [11,12] where Type II behaviour is reported.

### 3.4.4. CoGa

The  $V_{BV}$  value used by Kim is positive. Hence, we do not expect Type III behaviour. However, from Fig. 1(a) in [13], the behaviour is seen to be that of Type III. This is due to

- the additional multiplicative term that Kim had used which corresponds to the nonconfigurational (or phonon) part of the entropy and
- the relatively high temperature ( $\sim 0.48 T_c$ ) at which Kim had carried out his calculations.

However, for the interaction energies reported by Kim, when the calculations are carried out at 350 K (which corresponds to  $\sim 0.18 T_c$ ) without incorporating the nonconfigurational entropy contribution, the alloy shows Type II behaviour, as predicted. Hence, in Table 3, we have marked CoGa as a Type II alloy.

### 3.4.5. NiGa

The  $V_{BV}$  value used by Kim is negative. Hence, we can expect Type III behaviour to be predicted. However, from Fig. 1(a) in [9], the behaviour is seen to be that of Type IV. This is due to the relatively high temperature of  $\sim 0.25 T_c$  at which the calculations have been carried out. When the calculations are carried out at 700 K (which corresponds to  $\sim 0.16 T_c$ ), for the interaction energies reported by Kim, the alloy shows Type III behaviour, as predicted. So, in Table 3, we have marked NiGa to be a Type III alloy.

### 3.4.6. AuCd

The  $V_{BV}$  value used by Ren et al., and Ren and Otsuka is positive. Hence, we do not expect Type III behaviour to be predicted and this is confirmed by Fig. 1(d) in [11,12] where Type II behaviour is reported. We note, however, that previous experimental results have led AuCd to be classified as a Type I B2 intermetallic [2].

## 3.5. The size effect

Most of the B2 systems discussed above show Type II or Type III behaviour. We have shown in the previous section that the Type II and Type III behaviour result when the  $e_{BB}$  values are made comparatively repulsive. Thus, there exists a correlation between the Type II or Type III behaviour and the repulsive BB interaction (at least, within the framework of a nearest neighbour mean field model). The repulsive BB interaction may be understood in terms of the atomic size of the B species. In Table 4, we list the nearest neighbour distance in the various B2 intermetallics ( $D_1$ ), along with  $D_G = 2R_G$ , where  $R_G$  is the Goldschmidt radius of element B in its native crystal structure. Since  $R_G$  corresponds, roughly, to a minimum in the BB interaction potential, the ratio  $R = (D_G - D_1)/D_1$  quantifies the extent to which B atoms need to be 'squeezed together' if they are forced to be in neighbouring positions in B-rich intermetallic alloys in the B2 structure. A high value of  $R$  (say, 15% or more) might lead to a positive  $e_{BB}$  (due to the overlap of the cores of nearest neighbour B atoms) in the B2 phase, and hence a Type II or Type III behaviour may be expected.

From Table 4, we find that the nearest neighbour distances in NiAl, FeAl and CoAl are in range 2.47–2.51 Å while  $D_G = 2.86$  for aluminium; i.e.  $R$  values are

in the range 0.14–0.16. It is not surprising, then, that these intermetallics show a Type II or Type III behaviour experimentally ([2] and references therein).

For the other alloys in Table 4, the ratio  $R$  is positive indicating that B atoms would be squeezed together if they were to occupy nearest neighbour positions in B-rich alloys. However,  $R$  values for these alloys (between 0.06 and 0.09) are not as large as  $\approx 0.15$  for the aluminides. Thus, it is not clear whether the size effect would predict a Type II or Type III behaviour for these alloys. For example, the experimental situation is not clear for AuCd: it is traditionally believed to belong to Type I [2], though recent experimental study by [11,12] places it among Type II alloys. On the other hand, NiGa and CoGa are classified under Type III ([2] and references therein); since the size effect provides an insufficient explanation, electronic structure calculations (similar to [18] for NiAl) may throw more light on this issue.

#### 4. Conclusions

Using a nearest neighbour bond model under a mean field approximation, we have studied systematically the dependence of vacancy concentration in B2 intermetallics on alloy composition for different sets of interaction energies used in this model. We identified four generic types of behaviours exhibited by B2 intermetallics. In particular, we have derived a condition on the interaction energies for these systems to exhibit constitutional vacancies.

The results of all the prior mean field studies on NiAl, FeAl, CoAl, CoGa, NiGa and AuCd are rationalized within the framework of the classification presented in this study.

Although the same vacancy behaviour may be exhibited by systems with different sets of interaction energies, the behaviour of the other point defects are quite different. Therefore, experimental validation of theoretical results should include predictions on these other point defects too.

We have also examined how well the atomic size effect is able to explain the Type II or Type III behaviour in B2 alloys. While it provides a satisfactory explanation for the aluminides, it is inadequate for NiGa, CoGa and AuCd.

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#### References

- [1] C. de Novion, in: J.H. Westbrook, R.L. Fleischer (Eds.), *Intermetallic Compounds, Principles*, vol. 1, Wiley, New York, 1994, p. 559.
- [2] Y.A. Chang, J.P. Neumann, in: G.M. Rosenblatt, W.L. Worrell (Eds.), *Progress in Solid State Chemistry*, vol. 14, Pergamon Press, New York, 1983, p. 221.
- [3] G. Edelin, *Acta Metall.* 27 (1979) 455.
- [4] J.P. Neumann, *Acta Metall.* 28 (1980) 1165.
- [5] R. Krachler, H. Ipser, *Intermetallics* 7 (1999) 141.
- [6] R. Krachler, H. Ipser, K.L. Komarek, *J. Phys. Chem. Solids* 50 (11) (1989) 1127.
- [7] M.P. Gururajan, T.A. Abinandanan, 2000, *Intermetallics*, 8 (2000) 759.
- [8] M.P. Gururajan, T.A. Abinandanan, *Phil. Mag. A* (2001) in press.
- [9] S.M. Kim, *Acta Metall. Mater.* 40 (1992) 2793.
- [10] M. Kogachi, T. Haraguchi, *Intermetallics* 7 (1999) 981.
- [11] X. Ren, K. Otsuka, *Phil. Mag. A* 2 (2000) 467.
- [12] X. Ren, K. Otsuka, M. Kogachi, *Scripta Mater.* 41 (1999) 907.
- [13] S.M. Kim, *J. Phys. Chem. Solids* 49 (1) (1988) 65.
- [14] L.N. Larikov, V.V. Geichenko, V.M. Fal'chenko, *Diffusion Processes in Ordered Alloys*, Amerind Publishing Co. Pvt. Ltd., New Delhi, 1981, p. 16.
- [15] M.P. Gururajan, *Mean Field Study of Point Defects in  $\beta$ -NiAl*, M.Sc. Thesis, Indian Institute of Science, Bangalore, India, 2000.
- [16] T.B. Massalski, H. Okamoto, P.R. Subramanian, L. Kacprzak (Eds.), *Binary Alloy Phase Diagrams*, second edn, ASM international, The Materials Information Society.
- [17] E.A. Brandes, *Smithells Metals Reference Book*, sixth edn, Butterworths, London, 1983.
- [18] M. Meyer, M. Faehnle, *Phys. Rev.* 59 (9) (1999) 6072.