

# The anti-structural bridge mechanism for diffusion in ordered alloys of the B2 type

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The antistructural bridge mechanism has recently been proposed as a major contributor to diffusion at compositions away from stoichiometry in B2 ordered alloys/intermetallic compounds. In the present study the connectivity of the mobile atom distribution on the sublattices is first analysed using the authors' adaptation to ordered structures of Manning's formalism for diffusion in the random alloy. For percolation to occur, the analytical formalism predicts that the threshold concentration of antistructural (with respect to the sublattice) atoms must be greater than 0.273 at all levels of order. Computer simulation of the same model shows that for percolation to occur, the threshold concentration of antistructural atoms must be greater than 0.245 (for complete disorder) but this decreases to 0.13 (for complete order). This means that at the typically high levels of order observed in many ordered alloys and intermetallic compounds, the ASB mechanism cannot be a contributor to diffusion unless the overall composition is greater than 0.565. This composition is outside the stability range of most of these materials. © 1997 Elsevier Science Limited

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# **1. INTRODUCTION**

The B2 structure, sometimes called the CsCl structure, is among the most common structures taken by ordered alloys and intermetallic compounds. Diffusion in this structure is generally believed to be via the vacancy mechanism, the vacancies being unequally partitioned between the two sublattices  $\alpha$ and  $\beta$  which compose the structure. The atomic species A mainly occupies the  $\alpha$  sublattice while the atomic species B mainly occupies the  $\beta$  sublattice. It is generally assumed that diffusion takes place via nearest-neighbour jumps.<sup>1</sup> However, nextnearest neighbour jumps are also possible in principle as they are also in b.c.c. disordered alloys or even pure b.c.c. metals on account of the close proximity of the next-nearest neighbour. Indeed, in those B2-type alloys which permit structural vacancies, in the presence of triple defect disorder the B atom, say, may move via next-nearest neighbour jumps, i.e.  $\beta \rightarrow \beta$  if the so-called triple defect mechanism is invoked.<sup>2</sup> In the present paper we will focus on nearest-neighbour vacancy jumps.

Even with the vacancy mechanism, several subsets of this mechanism have been proposed. There are

of jumps (the 6JC mechanism) are possible.<sup>3</sup> The 6JC is a special sequence of vacancy jumps (from the very large number possible) in which the first three jumps lead to local disorder but the following three jumps lead to the restoration of order. Computer simulations have since made it clear that the 6JC mechanism certainly occurs but only at low temperatures at and near the stoichiometric composition.<sup>4,5</sup> When the concentration of, say, *B* atoms on the  $\alpha$  sublattice (i.e. antistructural atoms) is reasonably high, then it can be recognized that with the  $\beta$  sublattice as well, a substructure of *B* atoms could provide continuity across the structure with

the six-jump cycle (6JC) mechanism and the anti-

structural bridge (ASB) mechanism. With respect to the former, it was recognized quite early that for

tracer diffusion to occur in the highly ordered structure, only certain highly correlated sequences

provide continuity across the structure with vacancies able to migrate across it freely without producing disordering. This is the ASB mechanism.<sup>6,7</sup> It presumes, then, that the vacancies exchange exclusively with B atoms by nearest-neighbour jumps irrespective of sublattice. The key question then is how high does the concentration of such antistructural B atoms need to be in order

to provide such a continuous substructure. Kao and Chang<sup>6</sup> and Kao *et al.*<sup>7</sup> showed by semiquantitative arguments based on a small cell that the concentration of such antistructure atoms required to form a continuous substructure could be as low as 0.032. ('Concentration' here is defined as the number of *B* atoms divided by the number of sublattice sites). They then based a diffusion theory on the ASB mechanism and the 6JC mechanism to describe especially the compositional dependence of the tracer diffusion coefficients in a number of ordered alloy systems.

The calculation of the concentration of antistructure *B* atoms which form a continuous substructure together with the *B* atoms in the  $\beta$ sublattice is a site percolation problem. Below a critical concentration of antistructure *B* atoms this substructure is not continuous and long-range diffusion by the pure ASB mechanism is impossible though local diffusion may still occur. At the critical concentration of antistructure *B* atoms, the substructure become continuous and long range migration by the ASB mechanism can occur. Of course, at and above the critical concentration there will still be islands of *B* atoms which are not connected to the main (percolating) substructure.

The purpose of the present paper is to show by percolation arguments, backed up by computer simulation, that the concentration of antistructural atoms in fact needs to be much higher than that claimed by Kao *et al.*<sup>7</sup> to provide a continuous substructure. Our approach makes use of tracer diffusion as a dynamic probe of the percolating structure in order to determine the *percolation threshold* or *critical concentration of antistructural* B *atoms*. We make use of some of the arguments presented by Belova and Murch<sup>8</sup> and illustrated there for the *B1* structure.

# 2. ANALYTICAL DEVELOPMENT

We consider a lattice of N sites which is subdivided into two sublattices  $\alpha$  and  $\beta$  each consisting of the same number of sites  $N_{\alpha}(=N_{\beta})$ . The  $\alpha$  sublattice is mainly occupied by A atoms and the  $\beta$  sublattice mainly occupied by B atoms. We assume that diffusion occurs via nearest-neighbour vacancy jumps. We introduce four vacancy-atom exchange frequencies:  $w_A^{\alpha \to \beta}$  for A atoms jumping from the  $\alpha$ sublattice to the  $\beta$  sublattice,  $w_A^{\beta \to \alpha}$  for the reverse jump,  $w_B^{\beta \to \alpha}$  for B atoms jumping from the  $\beta$  sublattice to the  $\alpha$  sublattice,  $w_B^{\alpha \to \beta}$  for the reverse jump. These frequencies may be conceived as average jump frequencies or they may be explicitly given. This describes the ordered structure as a combination of two sublattices, each of which is a random distribution of A and B atoms but of course at a different composition.

The occupational variables are introduced as  $c_A^{\alpha} = N_A^{\alpha}/N_{\alpha}$ ,  $c_A^{\beta} = N_A^{\beta}/N_{\beta}$ ,  $c_B^{\alpha} = N_B^{\alpha}/N_{\alpha}$ ,  $c_B^{\beta} = N_B^{\beta}/N_{\beta}$ , where  $N_A^{\alpha}$  is the number of A atoms on the  $\alpha$  sublattice, etc.

The vacancy concentration is vanishingly small and therefore  $c_A + c_B \approx 1$ , where  $c_A$  and  $c_B$  are the overall compositions of A and B atoms. In order to define all four values of  $c_A^{\alpha}$ ,  $c_A^{\beta}$ ,  $c_B^{\alpha}$ ,  $c_B^{\beta}$  it is necessary only to introduce a single unknown variable: we let this be  $c_B^{\alpha}$ . We have that

$$c_A^{\alpha} = 1 - c_B^{\alpha}, \ c_A^{\beta} = 2c_A + c_B^{\alpha} - 1, \ c_B^{\beta} = 2c_B - c_B^{\alpha}$$
(1)

At equilibrium the number of jumps of A atoms in a long time t from the  $\alpha$  sublattice to the  $\beta$  sublattice must be equal to the number of reverse jumps, similarly for the B atoms. This, with eqn (1) leads to the occupation equation:

$$(1 - \epsilon^2)(c_B^{\alpha})^2 + [1 - 2c_B + \epsilon^2(1 + 2c_B)]c_B^{\alpha} - 2c_B\epsilon^2 = 0$$
(2)

where  $\epsilon$  is an especially convenient combination of frequencies such that

$$\epsilon^{2} = \frac{w_{A}^{\alpha \to \beta} w_{B}^{\beta \to \alpha}}{w_{B}^{\alpha \to \beta} w_{A}^{\beta \to \alpha}}$$
(3)

and  $0 \le \epsilon \le 1$  because by definition of the B2 structure above we have  $w_A^{\alpha \to \beta}/w_A^{\beta \to \alpha} \le 1$  and  $w_B^{\beta \to \alpha}/w_B^{\alpha \to \beta} \le 1$ . In other words, the frequency of disordering jumps is lower than reordering jumps for both components. Then, the positive root of eqn (2) is

$$c_B^{\alpha} = \frac{\sqrt{g} - 1 + 2c_B - \epsilon^2 (1 + 2c_B)}{2(1 - \epsilon^2)}$$
(4)

where  $g = (1 - 2c_B)^2(1 - \epsilon^2)^2 + 4\epsilon^2$ . Thus given  $c_B$ and  $\epsilon$  the occupations of the sublattices are completely determined from eqn (4) (and eqn (1)). It is clear now that: (a) when  $\epsilon = 1$  the concentration  $c_B^{\alpha} = c_B$  (directly from eqn (2)) and this is the completely disordered state; (b) when  $\epsilon = 0$  then  $c_B^{\alpha} = 0$ , if  $c_B \le 0.5$  and  $c_B^{\alpha} = 2(c_B - 0.5)$  if  $c_B > 0.5$ . This is the completely ordered state. Now we can introduce the long range order parameter S as follows:

$$S = \frac{c_I - c_I^i}{c_I},\tag{5}$$

where I = B,  $i = \alpha$  if B atoms are a minority component  $(c_B < 0.5)$ ; I = A,  $i = \beta$  if A atoms are a minority component  $(c_B > 0.5)$ . As was mentioned above, for the disordered state  $c_B^{\alpha} = c_B$ , this leads to  $\epsilon = 1$  and S = 0. In the completely ordered state  $c_B^{\alpha} = 0$  if  $c_B \le 0.5$  and  $c_B^{\alpha} = 2(c_B - 0.5)$  if  $c_B > 0.5$ . These are both equivalent to  $\epsilon = 0$  and S = 1.

The tracer correlation factor f is a quantity which describes correlation or memory between atomic jumps of a tracer atom. When f equals unity, each jump made by a tracer atom occurs in a random direction, i.e. there is no correlation between jumps and the tracer follows a random walk. On the other hand, when f equals zero, each jump made by a tracer atom is reversed and there can be no long-range diffusion. Above the percolation threshold there is long-range diffusion (though the jumps of a tracer may still be quite correlated) and  $0 < f \le 1$ . Below the percolation threshold the correlation factor will vanish because tracer atoms will be isolated in islands and be unable to undergo long-range diffusion.

Consider now the following expressions for the tracer correlation factors  $f_A$  and  $f_B$  for A and B atoms proposed by Belova and Murch<sup>9</sup>

$$f_A = \frac{H_1 H_2}{H_1 H_2 + H_1 w_A^{\beta \to \alpha} + H_2 w_A^{\alpha \to \beta}}$$

and

$$f_B = \frac{H_1 H_2}{H_1 H_2 + H_1 w_B^{\beta \to \alpha} + H_2 w_B^{\alpha \to \beta}} \tag{6}$$

where  $H_1$  is the escape frequency for vacancies on the  $\beta$  sublattice and  $H_2$  is the escape frequency for vacancies on the  $\alpha$  sublattice. In general case with Manning's<sup>10</sup> random alloy approximation in mind, the Hs have been shown to satisfy<sup>9</sup>

$$\frac{1-f_o}{2} = \frac{c_A^{\alpha} w_A^{\alpha \to \beta}}{2w_A^{\alpha \to \beta} + H_1} + \frac{c_B^{\alpha} w_B^{\alpha \to \beta}}{2w_B^{\alpha \to \beta} + H_1}$$

and

$$\frac{1-f_o}{2} = \frac{c_A^\beta w_A^{\beta \to \alpha}}{2w_A^{\beta \to \alpha} + H_2} + \frac{c_B^\beta w_B^{\beta \to \alpha}}{2w_B^{\beta \to \alpha} + H_2}$$

where  $f_o$  is the (geometrical) tracer correlation factor. In this structure  $f_o = 0.72722.^{11}$ 

Now let us describe the percolation behaviour. The physically accessible domain in the  $c_B^{\alpha}/c_B$  plane is shown in Fig. 1 by the bold outline triangle. It is formed as follows. When there is no distinction between sublattices, i.e. we simply have a random alloy (S=0), then  $c_B^{\alpha} = c_B$ . On the other hand when the lattice is always ordered as much as possible (S=1) then  $c_B^{\alpha} = 0$  for  $0 < c_B \le 0.5$  as all B atoms are on the  $\beta$  lattice. When  $0.5 < c_B < 1.0$  the  $\alpha$  sublattice then fills with B atoms.

The percolating part of this physically accessible domain can be found as follows: first we assume that  $w_A^{\alpha \to \beta}$  and  $w_A^{\beta \to \alpha}$  both are very small, such that

- 1. we can put  $w_A^{\alpha \to \beta} = 0$  and  $w_A^{\beta \to \alpha} = 0$  in eqn (7);
- 2.  $\epsilon$  can have any constant value from 0.0 to 1.0 and therefore any level of order is possible,  $c_B^{\alpha}$ now is the main parameter determining the possibility of percolation.

Then we have eqn (7) as follows:

$$\frac{1-f_o}{2} = \frac{c_B^{\alpha} w_B^{\alpha \to \beta}}{2w_B^{\alpha \to \beta} + H_1};$$

$$\frac{1-f_o}{2} = \frac{c_B^{\beta} w_B^{\beta \to \alpha}}{2w_B^{\beta \to \alpha} + H_2}$$
(8)

For the concentration  $c_B^{\alpha}$  we will then have that the critical condition for percolation (from the restriction  $H_{1(2)} > 0$ ) is

$$c_B^{\alpha} > 1 - f_o \tag{9}$$



Fig. 1. The physically accessible domain of  $c_B^{\alpha}$  versus  $c_B$ —bold-outline triangle.

Thus, for percolation to occur and the ASB mechanism to operate,  $c_B^{\alpha}$  must be greater than 0.273 (this is shown as the horizontal solid line in Fig. 1) and, of course,  $c_B^{\alpha}$  must also be in the physically accessible domain discussed above.

# **3. COMPUTER SIMULATION**

In order to assess the inequality (eqn (9)) Monte Carlo computer simulation was performed on the present model using exactly the same procedures as described in Ref. 4 (see also the more general review Ref. 12) but adapted in an obvious way to the case of the B2 structure. A level of order was specified, the configuration was frozen and a vacancy was inserted next to a B atom. B atoms were then permitted to diffuse. The (periodic) lattice size was 54000 sites (larger lattice sizes did not change the results), the number of jumps per Batom was at least 100 and runs were repeated until the equivalent of at least 10000 atoms of each type was averaged. The results were also averaged over 30 starting (frozen) configurations. The correlation factor was calculated from<sup>12</sup>

$$f_B = \frac{\langle \mathbf{R}_B^2 \rangle}{\langle n_B \rangle a^2} \tag{10}$$

where  $\langle \mathbf{R}_B^2 \rangle$  is the mean square displacement,  $\langle n_B \rangle$  is the average number of jumps per *B* atom and *a* is the elementary jump distance. The fractional standard error in the correlation factor was about 0.2%.

#### 4. SIMULATION RESULTS

In Fig. 2 we present typical results for the correlation factor of the *B* atoms as a function of  $c_B$  at various levels of order. Curve 1 represents the case when order is entirely absent (S=0) and the model then corresponds to the random alloy. We need to ignore the tails of the curves because they represent local diffusion only. The percolation threshold then occurs at the well-known value of  $c_B=0.245$ .<sup>13</sup> Incidentally, compositions below this were originally referred as the 'forbidden region' of the random alloy.<sup>10</sup> The result is slightly below the percolation threshold of  $1 - f_o$  predicted theoretically (see Fig. 1). Curve 4 represents the case when S=1. This corresponds to a completely filled  $\beta$ lattice with the excess *B* atoms distributed ran-



Fig. 2. Tracer correlation factor  $f_B$  as a function of  $c_B$ . Curve 1 corresponds to S=0.0, curve 2 to S=0.5, curve 3 to S=0.75 and curve 4 to S=1.0.

domly on the  $\alpha$  sublattice. The percolation threshold here occurs at  $c_B = 0.565$  (or  $c_B^{\alpha} = 0.13$ ). This is substantially less than  $c_B (= 1 - f_o/2) = 0.6364$  (i.e.  $c_{R}^{\alpha} = 0.273$ ) predicted analytically above. The discrepancy comes about in the following way. When  $c_B > 0.5$  the  $\beta$  sublattice is always full for S = 1. (B) atoms on this lattice are next nearest-neighbours.) Thus any additional B atoms appear on the  $\alpha$  sublattice and provide pathways between the next nearest-neighbours, thereby in effect magnifying the size of these B atoms in a percolation sense. This is not explicitly taken into account in the analytical formalism. Curves 2, 3 in Fig. 2 represent intermediate levels of order and give percolation thresholds between the above extremes. The percolation thresholds are plotted in Fig. 1. It is seen that they fall roughly on a straight line (shown as dashed). The area above this line and within the bold outline triangle (the physically accessible domain) is the percolation region.

Importantly, it is seen that for S=1 percolation is simply not possible until  $c_B > 0.565$ . Several constant S contours are shown within the domain of Fig. 1. They clearly indicate that lower levels of order (S < 1) will require even high values of  $c_B^{\alpha}$  for percolation. At S=1 the corresponding value taken by  $c_B^{\alpha}$  is 0.13 and this is almost four times higher than that predicted by Kao *et al.*<sup>7</sup> by semiquantitative arguments. It is now clear that for high levels of order the ASB mechanism (for B atoms) simply cannot play a role unless  $c_B > 0.56$ . This must put this mechanism completely out of consideration for any of the systems discussed by Kao *et al.*<sup>7</sup>

For completeness we also focus on stoichiometry  $(c_B=0.5)$  and determine what level of order is

required to 'activate' the ASB mechanism simply by increasing temperature. Inspecting Fig. 1 one sees that the (computer simulation) percolation threshold occurs at  $c_B^{\alpha} \approx 0.14$  when  $c_B = 0.5$ . From eqn (5) we see that this will occur when S=0.72. This is quite a low level of order and will occur fairly close to the order/disorder temperature if this exists in a given system. For example, in CuZn this level of order occurs at about  $400^{\circ}C^{14}$  (T<sub>c</sub> occurs at 460°C). There are limitations, of course, with this kind of analysis which focuses on a specialized mechanism such as the ASB. The ASB mechanism of itself does not provide a means for the order to actually change in an alloy. (The same can also be said about the 6JC mechanism.) Thus it must work in concert with other vacancy-based mechanisms. In our opinion, generalized vacancy diffusion mechanism formalisms,<sup>9,15–17</sup> have a much greater potential for providing an understanding of the complexities of diffusion in ordered structures because they implicitly include the 6JC and ASB mechanisms without being limited to them.

## 5. CONCLUSIONS

In this paper we have analysed the connectivity of the distribution of mobile atoms on the sublattices of an ordered alloy of the B2 structure. First we used an adaptation to the ordered structure of Manning's diffusion formalism in the random alloy. This gives a percolation threshold of 0.273  $(1-f_o)$  for the antistructural atom concentration at all levels of order. Next, computer simulation showed that the percolation thresholds actually range from 0.245 (S=0) to 0.13 (S=1). This means that for high levels of order the ASB mechanism cannot be a contributor to diffusion because the overall composition would be outside the stability range of most ordered alloys and intermetallic compounds. At low levels of order the ASB mechanism may be operative. For example, at the stoichiometric composition and with S < 0.72 the ASB mechanism clearly contributes to diffusion.

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