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Diffusion by anti-structure defects in non-stoichiometric intermetallic compounds with B2 and L1₂ structures

S V Divinski and L N Larikov

Institute for Metal Physics, National Academy of Sciences of Ukraine, 36 Vernadsky street, Kiev 142, 252142, Ukraine

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Abstract. Self-diffusion in non-stoichiometric intermetallic compounds with the B2 and L1₂ structures has been considered. It was shown that the thermal and compositional anti-structure defects substantially affect the diffusivity forming ‘anti-structural bridges’ for a vacancy migration without additional disordering of the intermetallic compound. While this contribution was found to have a percolation nature for both sublattices in the case of the B2 structures, the percolation is to be taken into account only for diffusion of the minor element in AB₃ intermetallic compounds with the L1₂ structure. The numerical calculations were carried out for the CoGa triple-defect intermetallic compound. Critical exponents and fractal characteristics of percolation clusters were estimated. Values of the threshold anti-structure defect concentrations are 0.049 ± 0.002 for B2 structures and 0.0347 ± 0.0008 for the α -sublattice of the AB₃ compound with the L1₂ structure. Owing to the temperature dependence of defect concentration the percolation threshold is temperature dependent also and, e.g., corresponds to Co_{52.4}Ga_{47.6} composition at $T = 1323$ K. The theoretical predictions are compared with experimental data.

1. Introduction

The diffusivity of intermetallic compounds has recently attracted much attention and the background knowledge is of practical importance. The ordered atomic structure of intermetallic compounds imposes some restrictions on diffusion mechanisms because the simple nearest-neighbouring jumps of a vacancy may obviously lead to disordering [1].

A six-jump cyclic mechanism of a vacancy movement, which retains the atomic order, was offered for the intermetallic compounds with the B2 structure [2, 3]. Later, this mechanism was extended for the intermetallic compounds with the FCC and HCP lattices and AB₃ composition [4, 5]. Arita *et al* have shown [6] that the correlation factor must be also taken into account and this effect changes the ratio of self-diffusivities of components. Note that the cyclic mechanisms are usually considered for fully ordered intermetallic compounds at a strict stoichiometric composition.

However, it is known that intermetallic compounds exist typically in a certain compositional range. For example, the deviation from the perfect stoichiometry (A₅₀B₅₀) for the B2 structures may reach tens of per cent [7]. To maintain the given ratio of sites of different types the structural defects (vacancies and/or anti-structure atoms) are created. Here, the term ‘anti-structure atom’ refers to an atom at an arbitrary site of the ‘foreign’ sublattice.

With deviation from the exact stoichiometric composition some other diffusion mechanisms can become more important. For example, the diffusion mechanisms in terms

of 'long' atomic jumps at second-nearest-neighbouring sites (within the same sublattice) or by vacancy–anti-structure atom complexes (triple defects) were offered [8]. However, it should be emphasized that these mechanisms may be pronounced at the stoichiometric composition also, since the cyclic six-jump rings demand too correlated sequences of jumps and this, in general, substantially decreases their probabilities. Moreover, there exists a given concentration of thermal defects at the stoichiometric composition too and this may change the relative contributions of different diffusion mechanisms.

The present work is aimed at describing a model of diffusion by the anti-structure defects in intermetallic compounds with the B2 and $L1_2$ structures. It will be shown that this contribution may have a percolation nature and calculations of relevant percolation characteristics will be initiated.

2. A model of diffusion by anti-structure defects

The presence of anti-structure defects has already been stated to change the diffusion properties of intermetallic compounds.

Let us first consider a binary intermetallic compound AB with the B2 structure. A scheme of this structure is presented in figure 1(a). The nearest-neighbouring jumps of atoms are the jumps between different sublattices and, thus, enlarge the free energy of the system leading to the formation of anti-structure defects.

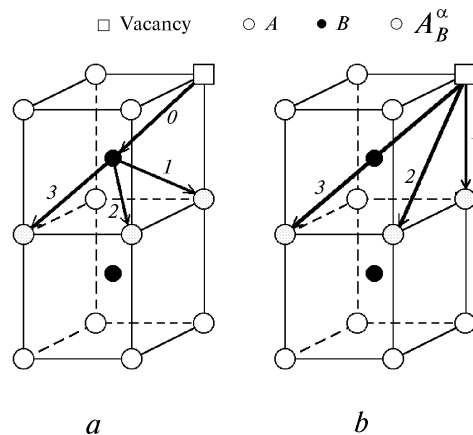


Figure 1. A scheme of nearest-neighbouring jumps of a vacancy in the B2 structure with the anti-structure defects (a) and the resulting jumps (b). Probable positions of anti-structure B atoms on the α -sublattice are indicated by A_B^α .

The presence of such defects allows us to suggest a new diffusion mechanism, that has been named as an anti-structural bridge (ASB) mechanism [9]. Let there be an anti-structure defect A_B^α (B atom at A site) at positions 1, 2, or 3 of the α -sublattice (the sublattice of A atoms) and a vacancy on this sublattice V^α (figure 1(a)). Then, the sequence of two jumps $0 + 1$, $0 + 2$, or $0 + 3$ will lead to the resulting jump of the vacancy on the α -sublattice retaining the given degree of order. This may be a jump into a site of the second coordination shell ($0 + 1$), third shell ($0 + 2$), or fifth shell ($0 + 3$), figure 1(b). It should be emphasized that contribution of this mechanism is different to the self- and impurity diffusion, because the movements of marked B atoms occur only on nearest-neighbouring distances from anti-structure positions on sites of the α -sublattice to sites of the β -sublattice.

We may generally state that the vacancy and the anti-structure atom exchange their positions. However, strictly speaking, initial and final anti-structure atoms are different atoms. Note that both these atoms contribute to the self-diffusion and only one (the given impurity atom) to the impurity diffusion.

If the concentration of anti-structure defects is rather high, they can form a connected network for a free vacancy migration without additional disordering of the intermetallic compound. Analysis shows that the activation of the ASB mechanism must have a threshold character. This was preliminarily checked in [10]. Here we extend our previous results for the B2 structures and examine the $L1_2$ structures.

So the ASB mechanism suggests that the anti-structural atoms can serve as ‘bridges’ for free vacancy migration without extra disordering of the intermetallic compound. The existence of a vacancy and an anti-structural atom at sites that are the nearest neighbours of a given atom in the second sublattice is the crucial factor at this, as shown above.

To provide diffusion on the macroscopic scales an infinite cluster must exist that connects ‘allowed’ for diffusion ‘bridges’ of the anti-structure atoms. Then, a vacancy bordering with the given cluster can migrate on large scales.

This consideration directly supports an idea about the percolation threshold—the mass transfer on large scales starts at a given critical concentration of ‘bridges’ built from the anti-structure atoms.

Note that in the case under consideration the percolation conditions differ markedly from those generally accepted for the cubic lattices. Indeed, while eight nearest-neighbouring β -sites are accessible for simple vacancy jumps, the vacancies V^α can move into 26 sites of the α -sublattice through the ASB mechanism (six sites on the second coordination shell + 12 on the third shell + eight on the fifth one). The same relation is true for the vacancy diffusion on the β -sublattice with the aid of anti-structure A atoms. This effect must substantially reduce the percolation threshold.

The offered ASB mechanism of diffusion can be thought of as ‘broken’ six-jump cycles, when the initial order is attained already after two jumps of a vacancy instead of six due to the existence of anti-structure defects *prior* to the diffusion act.

Now let us consider an AB_3 intermetallic compound with the $L1_2$ structure. It can be

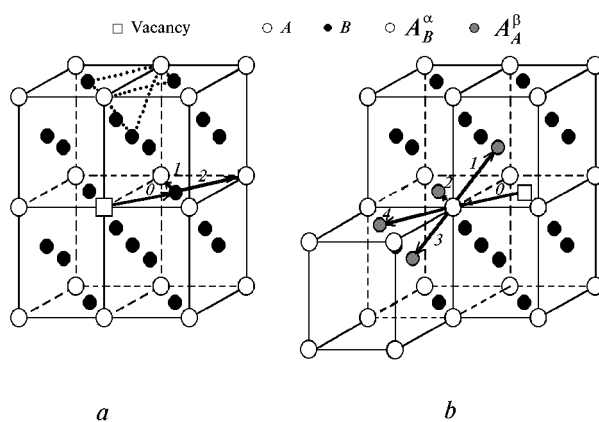


Figure 2. A scheme of nearest-neighbouring jumps of a vacancy on the α -sublattice (*a*) and on the β -sublattice (*b*) in the $L1_2$ structure. Probable positions of anti-structure A and B atoms on the β - and α -sublattices are indicated by A_A^β and A_B^α , respectively. Dotted lines present plane and bent trajectories of cyclic jumps.

sketched as follows (figure 2(a)): A atoms occupy the corners of a cubic lattice, and B atoms are placed at the face centres. This arrangement brings us to a principal difference in diffusion mechanisms for A and B atoms that is due to their different atomic environment. This was described even in [11]. Only B atoms are easily seen to be the nearest neighbours of A atoms (12 B atoms), whereas four A and eight B atoms are the nearest-neighbours of B atoms. In [4, 5] only cyclic movements were considered for the diffusion of A atoms, while a superposition of direct and cyclic jumps was suggested to contribute to diffusion of B atoms. Plausible trajectories of cyclic movements are presented in figure 2(b) by dotted lines. In this figure both plane and bent trajectories are denoted.

By the ASB mechanism the V^α vacancies can move into six next-nearest-neighbouring sites (the sequence of jumps $0 + 1$) and into 12 sites of the fourth coordinate shell ($0 + 2$), figure 2(a).

In contrast, the vacancies V^β can jump into eight nearest-neighbouring β -sites ($0 + 1$), four positions from the second coordinate shell ($0 + 2$), 16 sites of the third shell ($0 + 3$), and four positions from the fourth shell ($0 + 4$), figure 2(b). Note that the nearest-neighbouring β -sites can be accessible through both direct jumps and this, more sophisticated mechanism. At this point it should be noted that diffusion of the minor element in the AB_3 compound may be handled by two mechanisms: (i) nearest-neighbouring jumps of anti-structure A atoms on the B sublattice by B vacancies; and (ii) the ASB mechanism. While a given anti-structure A atom can jump into eight sites in way (i), $4 + 16 + 4 = 24$ sites are additionally available for the jumps of (ii) type. Thus, the ASB mechanism may play the most pronounced role for diffusivity of A atoms in AB_3 compounds with the $L1_2$ lattice.

Unlike the case of intermetallic compounds with the B2 structure, there is no clear percolation effect in the diffusivity of anti-structural A atoms on the β -sublattice due to coexistence of two diffusion paths ((i) and (ii)). Indeed, the anti-structure defects govern the self-diffusion at an arbitrary concentration, but increase of this concentration results in addition of the (ii) term to the simple (i) one. Note that the contribution of only mechanism (ii) is percolative one. However, it is likely to be impossible to 'subtract' this contribution from the integrated diffusion flow. On the other hand, the diffusion of anti-structural B atoms on the α -sublattice has a percolation nature and this will be further discussed in detail.

Let us determine the percolation probability P as a probability that a randomly chosen vacancy on a given sublattice can visit an infinite number of distinct sites of this sublattice by jumps through the ASB mechanism.

Then, the ASB contribution to the net diffusivity will be determined by:

$$D_A \sim f_{ASB} X_{\square}^{\beta} X_A^{\beta} P \quad (1)$$

and

$$D_B \sim f_{ASB} X_{\square}^{\alpha} X_B^{\alpha} P \quad (2)$$

where $X_{\square}^{\beta} = N_{\square}^{\beta}/N$ is the vacancy concentration on the β -sublattice and $X_A^{\beta} = N_A^{\beta}/N$ is the concentration of anti-structure A atoms; N is the total number of distinct sites on both sublattices; and similarly, $X_{\square}^{\alpha} = N_{\square}^{\alpha}/N$ and $X_B^{\alpha} = N_B^{\alpha}/N$; f_{ASB} is the correlation factor.

In the numerical experiment the percolation probability P was determined as $M(L)/L^3$. Here L is the lattice size (L^3 is the number of sites) and $M(L)$ is the number of sites belonging to the largest (percolate) cluster. The numerical calculations were carried out for the range of $31 \leq L \leq 251$. The averaging was performed over 10^4 distinct realizations.

3. Intermetallic compounds with the B2 structure

Let us numerically examine the percolation handled by the ASB mechanism on cubic lattices. We will consider a random distribution of anti-structure defects over lattice sites. This approximation is likely to be most reliable at least at low deviations from stoichiometry.

For numeric evaluations we have to introduce a compositional dependence of concentration of the anti-structure defects (X_B^α and X_A^β). This problem has been frequently treated [12, 13]. In any intermetallic compound at exact stoichiometric composition there is some, non-zero concentration of thermal defects. Constitutional defects are known to be formed besides the thermal defects with deviation from the stoichiometric composition. Several models have been suggested to determine their concentrations. These models start either from the mass-action laws between the defect concentrations, or from the principle of minimum free enthalpy of the crystal. In the present work we will use the results of [14] where the free enthalpy of the system was minimized by a Lagrange multiplier method.

It is well known that there are two main types of AB intermetallic compound. The first one is called an ‘anti-structural’ intermetallic compound where the dominant point defects are the anti-structure atoms on two sublattices. AuCd, AgMg, AuZn and other compounds belong to this type [15]. Concentrations of vacancies on both sublattices are very low in comparison with those of anti-structure atoms.

The second type is the ‘triple-defect’ intermetallic compounds. These are NiAl, CoGa, NiGa and others. In such intermetallic compounds the B atoms are larger than the A atoms. Anti-structure A atoms and vacancies with doubled concentration on the α -sublattice are the main thermal defects at the stoichiometry.

All present numerical evaluations were carried out for the Co-rich region of the CoGa triple-defect compound. Due to the thermal activation, a non-zero concentration of anti-structure Co atoms on the Ga sublattice (X) contributes to the diffusion by the ASB mechanism even at the stoichiometric composition.

The concentration X_{Co}^{Ga} of the Co anti-structure atoms and the concentration of vacancies X_{\square}^{Co} on the Co sublattice for the CoGa compound with composition Co_xGa_y ($y = 1 - x$ and $x > y$) are functions of temperature and composition. In [14] the following relations were derived:

$$(X_{\square}^{Co})^3 + s(X_{\square}^{Co})^2 = \frac{1}{4} \exp \left\{ -\frac{3Q}{kT} \right\} \quad (3a)$$

$$X_{Co}^{Ga} = \frac{1}{2}(s + X_{\square}^{Co}) \quad (3b)$$

where

$$s = \frac{N_{Co} - N_{Ga}}{N_{Co} + N_{Ga}} \quad (4)$$

$Q \cong 0.265$ eV; k and T are the Boltzmann factor and the temperature. The value of Q was determined from a least-squares fit of these two relations to the experimental data. Substituting $N_{Co} = x(N_{Co} + N_{Ga})$ and $N_{Ga} = (1-x)(N_{Co} + N_{Ga})$ in (4) we have $s = 2x - 1$. Then, the value of X_{Co}^{Ga} as a function of composition x can be determined by solving (3a)–(3b). After simple algebraic transformations we will have:

$$\begin{aligned} X_{Co}^{Ga} &= 0.5\{0.667s + [B + \sqrt{A}]^{1/3} + [B - \sqrt{A}]^{1/3}\} & \text{at } A = a \left[\frac{a}{4} - \left(\frac{s}{3} \right)^3 \right] \geq 0 \\ X_{Co}^{Ga} &= 0.5\{0.667s + 2(B^2 + A^2)^{1/6} \cos(\beta/3)\} & \text{at } A < 0. \end{aligned} \quad (5)$$

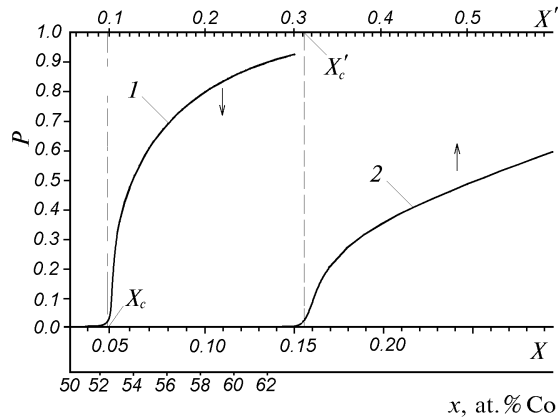


Figure 3. The percolation probability P as a function of concentration X of anti-structure atoms for the ASB mechanism (or deviation x from the stoichiometry at $T = 1323$ K for the CoGa compound) (curve 1) and that as a function of 'open bonds' X' for the percolation on the cubic lattice (curve 2). The percolation thresholds X_c for the ASB mechanism and X'_c for the 'standard' percolation are indicated.

Here, $B = a/2 - (s/3)^3$; $a = \frac{1}{4} \exp\{-3Q/kT\}$; $\cos \beta = B/\sqrt{B^2 + A^2}$. At the stoichiometric composition ($s = 0$) we will have a well known relation for the triple defects: $X_{Co}^{Ga}|_{s=0} = 0.5X_{\square}^{Co}|_{s=0}$.

Let us examine the conditions of appearance of the macro-diffusion when the anti-structure atoms must form a continuous bridge through the lattice.

Dependence of the percolation probability P on the concentration X of the anti-structure atoms is shown in figure 3, curve 1. To compare with well known results for 'standard' percolation on cubic lattices it is better to use a partial concentration X' that is referred to the ratio of the number of anti-structure atoms to the number of distinct sites on this sublattice ($X' \equiv 2X$, since we have equal numbers of sites on two sublattices). Relations (5) allow us to relate the anti-structure defect concentration X to composition of the CoGa compound. The bottom axis in figure 3 presents the relevant Co concentration x . These numeric evaluations were performed for $T = 1323$ K.

In the same figure we present the 'standard' dependence of P on the concentration X' (upper axis) of 'open bonds' at percolation on a 3D cubic lattice with six bonds for each site (curve 2).

The P value is small at low deviation from stoichiometry. The concentration of the anti-structure atoms grows with the deviation x from the stoichiometric composition, but the probability for a site to belong to the infinite cluster increases sharply only at x_c . If x further increases, the P value reveals nearly parabolic growth up to one. This behaviour differs strongly from standard one, where nearly linear growth up to one must be observed (see curve 2 in figure 3). Moreover, unlike the 3D percolation on a cubic lattice, only one percolate cluster is formed for the ASB mechanism in the B2 structure.

The critical concentration X_c (and, respectively, the critical composition x_c for a given temperature T) is determined as a greatest value of X (or x) at which the relation $P = 0$ remains valid within the errors of numeric calculations.

Analysis of results of numerical experiments (figure 3, curve 1) gives a well established power dependence of the percolation probability near the threshold:

$$P \sim (X - X_c)^\beta \quad \text{at } X > X_c \text{ and } X \rightarrow X_c. \quad (6)$$

Our calculations give for the percolation threshold of the ASB mechanism $X_c \cong 0.049 \pm 0.002$ ($x_c \cong 52.4 \pm 0.1$ at.% at $T = 1327$ K that corresponds to the deviation of $\sim 2.5\%$ from the stoichiometry at this temperature). The β -value depends crucially on the precise X_c value and shows large dispersion: $\beta \approx 0.8 \pm 0.4$. Further numerical calculations with increased size of computational lattice are needed to establish this value more precisely. To indirectly check our computations we have analysed a common case of well established percolation on a 3D cubic lattice (figure 3, curve 2) and have found that $\beta \cong 0.40 \pm 0.03$ and $X_c' \cong 0.312 \pm 0.001$. The later values agree well with the numerous theoretical and numerical data for the 'standard' percolation [16]. It is seen that the percolation threshold X_c for the ASB mechanism is substantially reduced in comparison with the 'standard' percolation value. This favours the activation of the ASB mechanism at low deviation from the stoichiometric composition. Such a behaviour is due to an enhanced number of bonds per site (26 instead of six, as shown in the previous paragraph). Our preliminary data also indicate that the β -value for the ASB percolation is likely to deviate substantially from the standard one. This may be due to the existence of only one percolative cluster as stated above.

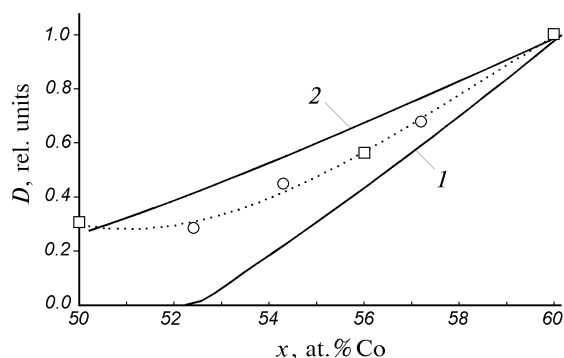


Figure 4. The compositional dependence of contribution of the ASB mechanism to the overall diffusion in CoGa compound with (1) and without allowing for the percolation (2). The dotted curve presents a polynomial fit to experimental data of Bose *et al* [8] (○) and Stolwijk *et al* [17] (□).

The percolation character of the ASB mechanism changes its contribution to the overall diffusion. In figure 4 we present these contributions calculated without percolation ($P \equiv 0.1$ in (1) and (2), curve 2) and by (1)–(2) (allowing for the percolation character of diffusion by the ASB mechanism, curve 1). In the same figure the experimental data of Bose *et al* [8] and Stolwijk *et al* [17] are presented also. Only relative values of diffusion coefficients (experimental and theoretical) are presented. They were calculated according to a relation: $D' = D/D_{max}$. This allows us to compare roughly the run of the experimental curve and that of partial contributions of the ASB mechanism calculated in different ways. The behaviour of the experimental curve is seen to be closer to curve 1 than to curve 2. Observed systematic deviation of the experimental data from curve 2 supports the results of percolation analysis.

The cyclic mechanism of Elcock and McCombie [2] that contributes to the diffusion near the stoichiometric composition must be included in the analysis to give more justified conclusions. The final comparison with experiment can be carried out only after this step.

An additional problem is presented by the calculation of the correlation factor f_{ASB} that is likely to depend on the concentration of anti-structure defects. This is planned to be done in subsequent papers.

The percolation threshold x_c depends obviously on temperature in view of the temperature dependence of anti-structure defect concentration. Note that X_c does not depend on temperature, since this value is determined by only geometric restrictions. In figure 5 the $x_c(T)$ dependence is drawn for the CoGa compound. Analysis shows that it can be approximated by:

$$x_c(\text{at.}\%) \cong 54.9 - 79.9 \exp \left\{ - \frac{3Q}{2kT} \right\} \quad (7)$$

where Q is the effective activation energy from (3)–(5).

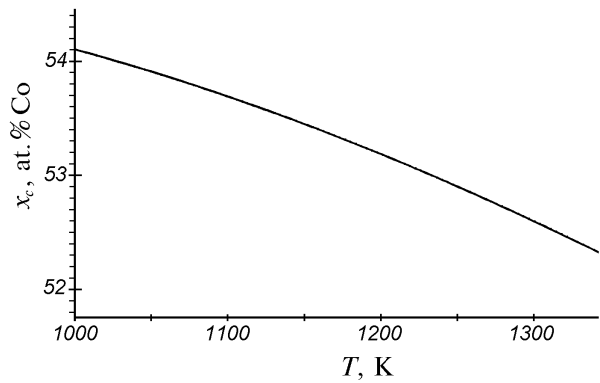


Figure 5. The temperature dependence of the Co concentration x_c corresponding to the percolation threshold X_c in the CoGa compound.

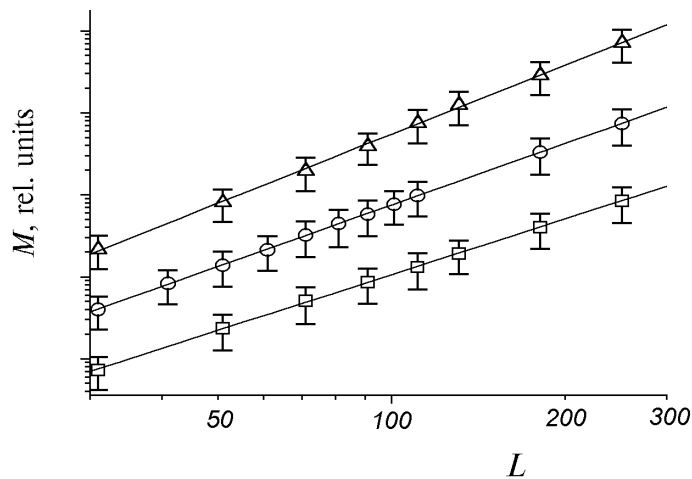


Figure 6. ‘Mass’ of greatest cluster M versus the lattice size L for different concentrations of anti-structure defects X near the percolation threshold: $X = 0.048$ (□); $X = 0.049$ (○); $X = 0.050$ (Δ). Error bars indicate the standard deviation of numerical data.

The percolation cluster at the percolation threshold is known to be a fractal object with a non-integer dimension D . The D value determines the scale behaviour of the ‘mass’ M of the greatest cluster for increasing lattice size L , $M(L) \sim L^D$. The mass M of a given cluster is defined as the number of distinct sites belonging to the cluster. In figure 6 the scale dependence of M is presented for three concentrations of the anti-structural defects near the threshold: $X_1 = 0.048 < X_c$, $X_2 = 0.049 = X_c$, and $X_3 = 0.050 > X_c$. Fitting to the linear M – L dependence in the log–log scale gives the dimensions D . The fractal dimension of the percolation cluster is 2.50 ± 0.12 at the threshold X_c [10]. Again, more precise calculations that are now in progress (with the lattice size about 500) must give a more justified value of D .

Summing up we can note that the percolation character of diffusion by the ASB mechanism must be taken into account to analyse the diffusivity of non-stoichiometric intermetallic compounds with the B2 structure. Since the relations (3a)–(3b) are not valid at large deviation from the stoichiometric composition, the anti-structure defect concentrations are overestimated in this region. Thus, a more reliable approximation than (3) will result in lower values of $P(x)$ at substantial deviation from the stoichiometric composition (or, respectively, at large defect concentration). This will further enhance the role of percolation at diffusion by the ASB mechanism.

4. Intermetallic compounds with L1₂ structure

Let us consider an AB₃ intermetallic compound with the L1₂ structure. As was stated above, the diffusion of anti-structure B atoms on the α -sublattice has a percolation character. Again, the percolation differs from the standard one on the cubic lattice. Indeed, there are 16 sites that can be accessible for a vacancy on the α -sublattice by a single step through the ASB mechanism.

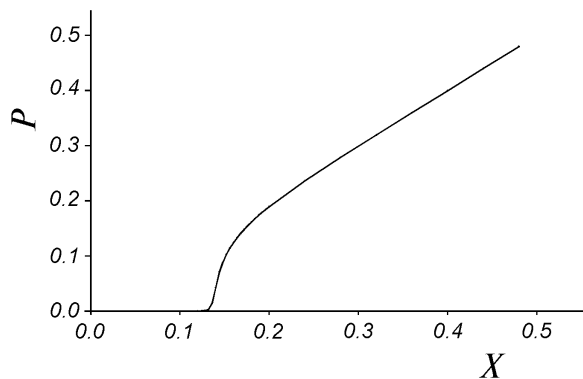


Figure 7. The percolation probability P as a function of concentration of anti-structure defects A_B^α on the α -sublattice for the ASB mechanism in the L1₂ structure.

The percolation probability P as a function of concentration of anti-structure defects on the α -sublattice is presented in figure 7. The percolation threshold corresponds to $X_c \cong 0.0347 \pm 0.0008$. Near the threshold P behaves as $\sim (X - X_c)^\beta$, $X > X_c$, with $\beta \approx 0.35 \pm 0.06$. As the deviation of anti-structure defect concentration from the threshold value X_c increases, nearly linear growth of P is observed (figure 7). This is similar to a common case of percolation on the cubic lattice.

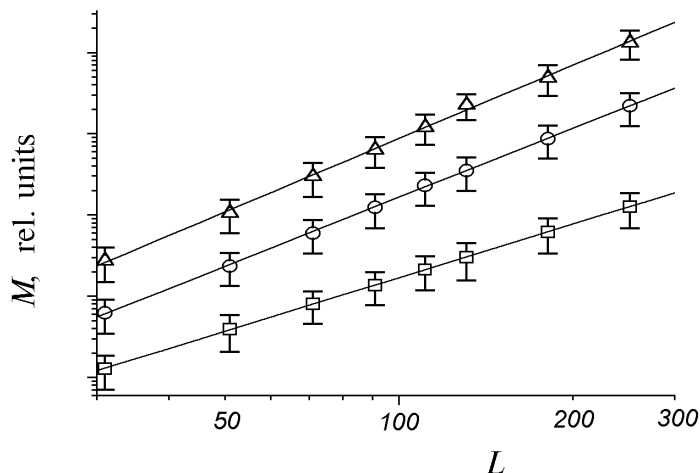


Figure 8. ‘Mass’ of greatest cluster M versus the lattice size L in the $L1_2$ structure near the percolation threshold: $X = 0.034$ (\square); $X = 0.0347$ (\circ); $X = 0.0349$ (Δ). Error bars indicate the standard deviation of numerical data.

Let us introduce a percolation cluster connecting all sites that can be visited by a vacancy through the ASB jumps. The analysis shows that this cluster is also a fractal object with dimension $D_f = 2.82 \pm 0.06$. The scale dependence of the ‘mass’ M of the greatest cluster near the percolation threshold is presented in figure 8. It is seen that this dependence obeys a power law $M \sim L^D$. At the percolation threshold $D = D_f < 3$, where 3 is the real space dimension. At $X > X_c$, $D \equiv 3$. Slight deviation from this value in our calculations ($D \cong 3.002 \pm 0.007$ at $X = 0.0349$) is due to the errors of numeric calculations.

The ASB mechanism gives also a strong contribution to the diffusivity of anti-structure A atoms on the β -sublattice. However, this contribution has no percolation character, since all anti-structural bridges are now connected by simple nearest-neighbouring jumps of A_B^α into V^β vacancies.

This ASB mechanism must be taken into account to re-examine the ratio of diffusivities of constitutional atoms in AB_3 compounds. This will be done in next paper, where the comparison with experiment on Ni_3Al will be carried out.

5. Summary

In the present work it was shown that the anti-structure defects give a pronounced contribution to the diffusivity of intermetallic compounds with the B2 and $L1_2$ structures. This contribution has mainly a percolation nature and introduces a power term $\sim (X - X_c)^\beta$ into the diffusivity near the percolation threshold X_c , $X > X_c$.

Such a behaviour is an intrinsic feature of ordered intermetallic compounds, both crystalline and quasicrystalline. To compare these results with the experiment we must also consider all other diffusion mechanisms (mainly cyclic ones) that contribute to the diffusion at the stoichiometric composition. Note that the six-jump-ring mechanism of Elcock and McCombie changes to ten-jump rings for the quasicrystal intermetallic compounds [18].

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