DIFFUSION IN THE Ti–Al SYSTEM

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Abstract—Many properties of industrial Ti–Al alloys, such as high-temperature stability of the lamellar structure and creep resistance, are determined by diffusion rates in the phases and along the interfaces. The knowledge of diffusion characteristics and fundamental understanding of diffusion mechanisms are of great importance to the research and design of industrial Ti–Al alloys. This paper gives an overview of recent progress in experimental and theoretical studies of diffusion behavior in the phases of the Ti–Al system. The experimental methods used in modern diffusion measurements are briefly described, and recent experimental results for Ti and Al diffusion in α-Ti(Al), β-Ti(Al), and intermetallic phases α2-Ti3Al and γ-TiAl, are summarized. The results for interdiffusion and impurity diffusion in these phases are also discussed in detail. The second part of the paper provides an overview of current understanding of point defects and diffusion mechanisms in Ti3Al and TiAl. A statistical model of point-defect disorder in ordered compounds is presented and applied to Ti3Al and TiAl using input data generated with embedded-atom potentials. Possible atomic mechanisms of diffusion in these compounds are analyzed in detail, and methods of diffusion calculations under different mechanisms are reviewed. The relative importance of different mechanisms in Ti3Al and TiAl is evaluated by comparing their estimated activation energies. Prospective topics of further experimental and theoretical research in this area are outlined.

Keywords: Intermetallic compounds; Diffusion; Radio-tracer method; Theory and modeling

1. INTRODUCTION

Intermetallic compounds of the Ti–Al system and alloys based on such compounds are materials of rapidly growing technological importance. Such alloys have a relatively high yield strength at elevated temperatures, advanced creep characteristics, and good oxidation/corrosion resistance [1, 2]. This combination of useful properties makes them very attractive as high-temperature structural materials for aerospace, automotive and other applications. The knowledge of diffusion characteristics and the understanding of diffusion mechanisms in different phases of the Ti–Al system are of great importance to the entire area of research and design of Ti–Al alloys. Indeed, the alloys of this system that have a potential for industrial applications possess a two-phase structure consisting of alternating γ-TiAl and α2-Ti3Al lamellae. The formation and high-temperature stability of this lamellar structure are controlled by diffusion processes in the constituent γ and α2 phases, as well as along the semi-coherent γ/γ’ lamellar boundaries and γ/α2 interphase boundaries. Moreover, the creep resistance of the lamellar structure is also determined by diffusion characteristics of both the bulk phases and the interphase boundaries.

The current understanding of diffusion processes in the Ti–Al system is very incomplete. Experimental data on Ti and Al diffusion in Ti aluminides are scarce, and the knowledge of the respective atomic mechanisms of diffusion is very poor. Experimental studies of diffusion in the Ti–Al system are hampered primarily by the unavailability of suitable and inexpensive radioactive isotopes of Ti and Al. 44Ti is the only suitable radiotracer for Ti, but it is produced by a nuclear reaction at a cyclotron and its production in quantities needed for diffusion measurements requires rather long radiation times. The only suitable isotope of Al, 26Al, is also a cyclotron product. It is even more
difficult to produce and work with than $^{44}$Ti and, in addition, has very low specific activity.

We have recently initiated a broad program of extensive experimental and theoretical studies of diffusion phenomena in the Ti–Al system. Such studies will include lattice diffusion in the phases of this system, as well as diffusion along grain and interphase boundaries. The purpose of this article is to review the recent progress in this area, including the latest results obtained by our groups.

Section 2 provides a short description of the experimental methods applied for diffusion measurements in the Ti–Al system. In Section 3 we review the experimental information on self-diffusion, impurity diffusion and interdiffusion in α-Ti and β-Ti, as well as in the intermetallic compounds $\alpha_2$-Ti$_3$Al and γ-TiAl. Along with the most recent results of diffusion measurements, some earlier work is also discussed when appropriate. In the following two sections we review the recent advances in theoretical studies of point defects (Section 4) and diffusion mechanisms (Section 5) in intermetallic compounds of this system. In Section 6 we summarize and outline some prospective topics of future research.

2. EXPERIMENTAL METHODS OF DIFFUSION MEASUREMENTS

For a better understanding of the experimental results discussed in the next section it seems appropriate to give a brief summary of modern experimental methods applied in diffusion measurements. For further experimental details the reader is referred to original publications.

Ti self-diffusion measurements in Ti–Al alloys and compounds employ the radiotracer $^{44}$Ti and the serial sectioning technique. The $^{44}$Ti isotope is produced via the nuclear reaction $^4$Sc(p, 2n)$^{44}$Ti at a cyclotron, followed by a radiochemical separation of $^{44}$Ti from the Sc-target. This isotope is used in diffusion experiments in the form of an acid solution, a small amount of which is dropped (or evaporated in special cases) onto the polished surface of the sample to create a diffusion source. Diffusion anneals are performed in high-vacuum conditions with an accurate temperature control. The diffusion anneal is followed by the serial sectioning, the procedure in which thin layers of the material are removed from the sample parallel to the source surface. Depending on the ductility of the material, the sectioning can be performed with a microtome or by grinding the sample with a precision grinding machine (mechanical sectioning) [3–9]. The thickness of each removed layer is determined from the known density of the material and the sample weight reduction, measured with a microbalance. The radioactivity of the removed section is determined by measuring the rate of radioactive decays in the removed chips or on the grinding foil. Such measurements are performed with a well-type intrinsic-Ge γ-detector connected to a high resolution multichannel analyzer. The specific activity of the section, calculated from its thickness and its measured total activity, is proportional to the tracer concentration at the respective diffusion depth. The results of sectioning measurements on each sample are represented as a so-called penetration profile, i.e. a plot of the tracer concentration $c$ as a function of the penetration depth $x$. The spatial resolution of the profile obtained by mechanical sectioning is a few micrometers, while the depth of the profile is typically 50–200 µm. Alternatively, the sectioning can be performed by ion-beam sputtering [10]. In this method, the material sputtered with an Ar$^+$ ion beam is collected on a plastic film using a camera-type drive with an equal sputter time per each section. The sputter rate is maintained constant and is calculated from the total sputter time and the final crater depth. The plastic film is cut into pieces corresponding to individual sections, and the radioactivity of each piece is measured as described above. The spatial resolution of the method is around 0.1 µm, while the maximum depth of analysis is about 5 µm.

Depending on the availability of suitable isotopes and other factors, the radiotracer sectioning methods can be also applied for studying impurity diffusion in the Ti–Al phases (e.g. Refs [11–13]). The experimental procedures are essentially the same as described above, with two possible variations: (1) the tracer source at the sample surface is often created by evaporation in vacuum, and (2) in case of a β-emitting isotope, the radioactivities of the sections are measured with a liquid scintillation counter.

In many situations, particularly when a suitable radioisotope is not available, impurity diffusion can be successfully measured by secondary ion mass spectrometry (SIMS) [10, 13]. The in-depth profiling is implemented using a primary beam of high-energy O$_2^+$ ions. The maximum depth of analysis by this method is about 10 µm. For much deeper penetration depths, a so-called step-scan variant of the method can be applied. In this case, an oblique section of the diffusion zone is made by polishing, and the SIMS analyses are taken every 20 µm along the surface of this section. The depths in the measured penetration profile are later scaled according to the inclination angle of the section relative to the specimen surface. This method gives access to diffusion penetrations as deep as a few hundreds of micrometers. The SIMS technique is also applied for the analysis of impurity contents in the samples prior to diffusion measurements, regardless of the method employed afterwards for such measurements. The effect of spurious impurities on diffusion is a critical issue in many studies of the Ti–Al system, especially in α-Ti.
The diffusion coefficient $D$ can be deduced from the measured penetration profile knowing the diffusion time $t$. Depending on the surface conditions, there can be two types of penetration profiles. For instantaneous source conditions, which are most commonly encountered in diffusion experiments, the profile is described by a Gaussian function, $c \propto \exp(-x^2/4Dt)$. Thus, the plot $\ln c$ vs $x^2$ should be a straight line, and the diffusion coefficient can be determined from the slope of that line. For constant source conditions, the profile is described by a complimentary error function, $c = c_0 \text{erfc}(x/2\sqrt{Dt})$. The plot $\text{erfc}^{-1} c/c_0$ vs $x$ should be a straight line ($c_0$ being the surface concentrations), and the diffusion coefficient can again be determined from the slope of that line.

Interdiffusion measurements also provide very useful information, especially when they are performed on single-phase samples [4–6, 14]. Mirror-flat surfaces of two alloy samples, whose compositions lie within the homogeneity range of the phase, are welded together by annealing for a relatively short time with or without some mechanical pressure applied to the couple in order to improve the contact. The welded couples are then subject to longer diffusion anneals at desired temperatures. After the anneal, each couple is cut perpendicular to the bonding surface, and the chemical composition across the bonding surface is measured by electron probe microanalysis. The interdiffusion coefficient $D$ is determined, as a function of composition, by processing the measured concentration profile by the Boltzmann–Matano method [15]. The single-phase interdiffusion method can also be applied for studying interdiffusion between Ti or a Ti–Al phase, on one hand, and a foreign solute, on the other hand. For example, Sprengel et al. [16] have recently applied this method for measuring interdiffusion in single-phase $\beta$-Ti(X) couples ($X = \text{Cr, Mo or V}$). Some groups studied interdiffusion in Ti–Al phases by using multiphase diffusion couples (e.g. Refs [17–19]). Although such studies do provide interesting insights into different aspects (such as the Kirkendall effect, kinetic phase equilibria, etc.), the obtained interdiffusion coefficients can be significantly affected by short-circuit diffusion in the phase layers, non-equilibrium vacancy Fig. 1. Phase diagram Ti–Al [20].
concentrations, reaction kinetics at the phase boundaries, and other factors.

3. EXPERIMENTAL RESULTS

Figure 1 shows the latest version of the Ti–Al phase diagram. This version combines the previous versions with the new interphase lines obtained by Kainuma et al. [20] by the diffusion couples technique. According to this diagram, Al strongly stabilizes the α phase and extends its domain of existence towards larger Al contents (30–50 at.%) and higher temperatures (1400–1750 K). In this section we will discuss diffusive properties of several most important phases of the diagram. Their crystalline structures are shown schematically in Fig. 2.

3.1. Diffusion in terminal phases

3.1.1. Diffusion in α-Ti

3.1.1.1. Ti Self-diffusion. Self-diffusion in the h.c.p.-structure of Ti (α-Ti, see Figs 1 and 2) has not been well understood until very recently. Together with two other group IV B h.c.p. metals, z-Zr and z-Hf, α-Ti is classified as an “open” metal. In such metals the ionic-to-atomic radius ratio is unusually large in comparison with “normal” h.c.p. metals, such as Mg, Zn and Cd. Some metallic impurities (particularly Fe, Co and Ni) dissolve in “open” metals interstitially and diffuse anomalously fast by an interstitial mechanism [21]. Furthermore, such fast-diffusing impurities strongly accelerate self-diffusion in the matrix material. Both effects are especially pronounced in α-Zr, but are also quite significant in α-Ti. The strong impurity effect makes self-diffusion studies in these metals very problematic, because the self-diffusion coefficients measured on a nominally pure material may represent the extrinsic (i.e. fast-impurity controlled) rather than intrinsic diffusion. In our earlier work [8] we made an attempt to determine self-diffusion characteristics in α-Ti by radiotracer measurements on a relatively pure material (about 50 ppm Fe). The obtained diffusion coefficients turned out to be too high to be consistent with normal diffusion behavior in h.c.p. metals. In principle, one could conclude that intrinsic self-diffusion in α-Ti is anomalously fast, and even try to explain this behavior by some peculiarities of lattice dynamics in this phase. Alternatively, it was suggested [22] that the measurements of Ref. [8] were actually made in the extrinsic regime. Under this assumption, the intrinsic self-diffusion characteristics of α-Ti remained essentially unknown, and the question of whether they are normal or abnormal remained open.

More recently, self-diffusion in α-Ti was re-measured using four Ti materials with different impurity contents, including an ultrapure material with very low concentrations of Fe (0.02 ppm), Co (0.007 ppm) and Ni (<0.015 ppm) [10]. The 44Ti radiotracer and ion-beam sputtering were applied in that study. The diffusion coefficients obtained on the ultrapure material followed the Arrhenius law

\[ D = D_0 \exp(-Q/k_B T) \]

\( (k_B \) being Boltzmann’s factor) in the temperature range \( T = 873–1133 \) K, with the pre-exponential factor \( D_0 = 1.35 \times 10^{-3} \) m²/s and the activation energy \( Q = 3.14 \) eV. These parameters were

Fig. 3. Arrhenius diagram of self-diffusion in ultrapure \( \alpha \)-Ti measured on single-crystalline samples perpendicular (●) and parallel (○) to the c axis [10]. The results of previous measurements [8] in nominally pure α-Ti are shown for comparison (dotted line). The \( \alpha/\beta \) transition temperature is indicated.
measured on single-crystalline samples in the direction perpendicular to the $c$ axis. Diffusion along the $c$ axis, measured at two temperatures, was found to be a factor of two slower (Fig. 3). Importantly, all these diffusion coefficients are significantly lower, and the diffusion activation energy is higher, than those measured in our previous work [8]. Furthermore, the measurements on less pure materials always gave enhanced $D$ values in comparison with those obtained on the ultrapure material [10]. These observations confirmed that the previous studies indeed dealt with an impurity-enhanced, and not intrinsic self-diffusion in $\alpha$-Ti. On the other hand, it was shown [10] that the results obtained on the ultrapure material undoubtedly represented the intrinsic self-diffusion. Indeed, the extremely small impurity concentrations in the ultrapure material made the impurity effect highly unlikely. Also, the obtained Arrhenius parameters nicely follow the empirical rules established for “normal” h.c.p. metals [23]. Moreover, these parameters are very consistent with the latest measurements of self-diffusion in $\alpha$-Hf [24] and $\alpha$-Zr [25], which were also performed on very pure materials. Thus, these three “open” metals actually have quite normal self-diffusion characteristics, and in particular scale with the melting temperature together with “normal” h.c.p. metals (Fig. 4). It was also found that both “open” and “normal” h.c.p. metals follow a common correlation between the $c/a$ ratio of their lattice and the anisotropy ratio $D_L/D_T$ of self-diffusion [10], namely that $D_L/D_T > 1$ when $c/a < 1$ and vice versa.

3.1.1.2. Impurity Diffusion. Al impurity diffusion in $\alpha$-Ti was studied by the SIMS method in the same set of Ti-materials as those employed in self-diffusion measurements [10]. The diffusion coefficients in ultrapure $\alpha$-Ti were measured in the direction perpendicular to the $c$ axis over the temperature range 935–1140 K. They were found to follow the Arrhenius relation (1) with $D_0 = 6.6 \times 10^{-3}$ m$^2$/s and $Q = 3.41$ eV (Fig. 5). In this temperature range, Al diffusion is a factor of 3–6 slower than Ti self-diffusion. In both cases, however, the diffusion anisotropy ratio $D_L/D_T$ is about two (cf. Figs 3 and 5), which fits well into the $D_L/D_T = D_k$ vs $c/a$ correlation for h.c.p. metals mentioned above [10]. These data obviously represent the intrinsic diffusion behavior of Al. The latter shows all signs of normal substitutional diffusion dominated by the vacancy mechanism. Al diffusion measurements performed in Ref. [10] on less pure Ti materials gave significantly higher diffusion coefficients, which approached the results of earlier measurements made on a 99.9% Ti material [26]. This trend gives another confirmation that ultra-high purity is of critical importance for obtaining intrinsic diffusion characteristics of $\alpha$-Ti.

Diffusion of several other impurities in $\alpha$-Ti was

![Image](image_url)

**Fig. 4.** Normalized Arrhenius diagram of self-diffusion in h.c.p. metals [10]. The dashed lines border the zone defined by the empirical correlation $Q = 17.3RT$ established for group II h.c.p. metals [23]. The pre-exponential factors were assumed to lie between $2 \times 10^{-4}$ and $2 \times 10^{-5}$ m$^2$/s.

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**Fig. 5.** Arrhenius diagram of Al impurity diffusion in ultrapure $\alpha$-Ti measured on single-crystalline samples perpendicular (●) and parallel (○) to the $c$ axis [10]. The results of previous measurements [8] in a less pure $\alpha$-Ti are shown for comparison (dotted line). The $\alpha/\beta$ transition temperature is indicated.
investigated by different groups, and the results can be briefly summarized as follows. All impurities studied so far can be divided into two clearly distinct classes, which can be called normal impurities and fast impurities. Along with Al, the class of normal impurities includes Zr [27, 28], Hf [29, 30] and Au [31], as well as the recently studied In and Ga [32–34]. Their diffusion coefficients in α-Ti are close to those of Ti within approximately an order of magnitude (Fig. 6). The observed relation between the diffusion coefficients, $D_{\text{Ga}} > D_{\text{Ti}} > D_{\text{Al}} > D_{\text{In}}$, correlates with the relation between the respective atomic radii (Table 1). This behavior, as well as the respective Arrhenius parameters and the diffusion anisotropy, suggest that these impurities dissolve in α-Ti almost exclusively substitutionally and diffuse by the vacancy mechanism. The class of fast impurities includes Fe, Co and Ni [35, 36]. Their diffusion coefficients are close to one another (again, within approximately an order of magnitude), but are about 7–8 orders of magnitude greater than those for normal impurities (Fig. 7). Interestingly enough, the relationship between $D_{\perp}$ and $D_{||}$ for fast impurities is $D_{\perp} < D_{||}$, which is the opposite to what is observed for normal impurities. As was pointed out above, the fast impurities are most likely to dissolve in α-Ti interstitially and migrate by the direct interstitial, or some other interstitial-related mechanism. There are other impurities, like Cr and Mn [36], which probably also belong to the same class. They diffuse about two orders of magnitude slower than Fe, Co and Ni, but still too fast to be consistent with a normal vacancy mechanism. The non-metallic impurities C [37], O [38] and N [39] are also fast diffusers in α-Ti, and presumably diffuse by an interstitial mechanism as well. In some aspects, however, their diffusion behavior is different from that of transition-metal impurities. For carbon, for example, the diffusion anisotropy has the same sense as that for normal metallic impurities, namely $D_{\perp} > D_{||}$ [37].

### 3.1.1.3. Interdiffusion

All self-diffusion and impurity diffusion measurements discussed so far were made on pure α-Ti. No data are available for diffusion in the α-Ti(Al) solid solution within the low-temperature domain of its existence (Fig. 1). As far as the recently-discovered high-temperature (high-Al) domain is concerned, interdiffusion measurements have been recently performed at temperatures 1442, 1542 and 1591 K using multiphase diffusion couples [17]. The obtained diffusion coefficients show a ten-

![Fig. 6. Arrhenius diagram of impurity diffusion of Ga, Al and In in ultrapure α-Ti in comparison with Ti self-diffusion [33]. The α/β transition temperature is indicated.](image)

![Fig. 7. Arrhenius diagram of fast impurity diffusion in α-Ti in comparison with Ti self-diffusion.](image)

<table>
<thead>
<tr>
<th>Diffuser</th>
<th>$D_0$ (m²/s)</th>
<th>$Q$ (eV)</th>
<th>$r$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>$2.1 \times 10^{-3}$</td>
<td>3.06</td>
<td>0.135</td>
</tr>
<tr>
<td>Al</td>
<td>$6.6 \times 10^{-3}$</td>
<td>3.41</td>
<td>0.143</td>
</tr>
<tr>
<td>In</td>
<td>$3.1 \times 10^{-3}$</td>
<td>3.41</td>
<td>0.157</td>
</tr>
<tr>
<td>Ti</td>
<td>$1.4 \times 10^{-3}$</td>
<td>3.14</td>
<td>0.147</td>
</tr>
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dency to increase, and the activation energy to decrease, with increasing Al content.

3.1.2. Diffusion in β-Ti

3.1.2.1. Ti Self-diffusion. The b.c.c. phase of Ti (β-Ti, see Figs 1 and 2) demonstrates an anomalous self-diffusion behavior illustrated in Fig. 8. The self-diffusion coefficients, measured with the radiotracer ⁴⁴Ti and the mechanical sectioning method [9], clearly show a non-Arrhenius temperature dependence with a distinct upward curvature. This kind of anomalous behavior is a common feature of diffusion in group IV b.c.c. metals and their alloys. It was suggested [40] that this behavior is caused by a temperature dependence of the vacancy migration energy, arising from a softening of certain phonon modes that assist vacancy jumps. A phonon softening of this type is typical of many b.c.c. metals and alloys. This explanation was qualitatively confirmed by experimental measurements of phonon dispersion curves at elevated temperatures (see Ref. [41] for a review) and by the theoretical calculations [42]. Based upon the notion of a temperature-dependent vacancy migration energy, the self-diffusion data shown in Fig. 8 were approximated by a generalized Arrhenius equation [40]

\[ D = D_0 \exp\left(-\frac{Q}{k_B T}\right) \exp\left(\frac{\alpha}{k_B T^2}\right) \]  

The three fitting parameters of this equation were found to be \( D_0 = 3.53 \times 10^{-4} \text{ m}^2/\text{s} \), \( Q = 3.40 \text{ eV} \) and \( \alpha = 1335 \text{ eVK} \). For a quantitative explanation of the strong curvature observed in Fig. 8, the vacancy formation energy must also be considered as temperature-dependent. The anomalous temperature dependence of Ti self-diffusion pertains in β-Ti(Al) alloys. The recent ⁴⁴Ti self-diffusion measurements in β-Ti₉₀Al₁₀ and β-Ti₇₀Al₃₀ [6] gave diffusion coefficients very close to those in pure β-Ti. In particular, they also show an upward curvature in the Arrhenius plot (Fig. 9). Ti self-diffusion was also studied in concentrated β-Ti(X) alloys, X being a β-stabilizing element other than Al. Some elements have only a weak or no effect on Ti self-diffusion, being in this respect similar to Al. On the other hand, Cr [43], Mo [43] and V [44] strongly decrease the mobility of Ti. It should be mentioned that Mo itself is a slow diffuser in β-Ti, while Cr is a fast diffuser [45].

3.1.2.2. Impurity Diffusion. Al impurity diffusion coefficients in β-Ti were first determined by Araki et al. [46]. As a part of their interdiffusion study in diluted β-Ti(Al) alloys, they calculated the impurity diffusion coefficients by extrapolating their \( \tilde{D} \) values towards zero aluminum concentration. These data indicate that Al diffuses in β-Ti about a factor of two slower in comparison with Ti self-diffusion (Fig. 8). As was discussed in Section 3.1.1, Al is a relatively slow diffuser also in α-Ti, although the
difference between the diffusivities of Al and Ti in z-Ti is larger than in β-Ti. Obviously, Al diffuses in β-Ti by the vacancy mechanism, with interactions between Al atoms and vacancies being slightly repulsive. Because the measurements of Araki et al. [46] covered a relatively narrow temperature range, no curvature of the Arrhenius plot was detected. More recently, Al diffusion coefficients in β-Ti were determined by SIMS measurements [24]. The results of these new measurements are in very good agreement with the data of Araki et al., but extend them to a wider temperature range. Taking the results of these two studies together, it is clear that Al diffusion does show a pronounced non-Arrhenius temperature dependence similar to that of Ti self-diffusion (Fig. 8).

As far as other impurities in β-Ti are concerned, diffusion coefficients of Ga and In [47] were found to be rather close to those of Al and Ti, and to show the same upward curvature in the Arrhenius plot (Fig. 8). As was pointed out in Section 3.1.1, diffusion characteristics of these group III A impurities in z-Ti are also similar to those of Ti. Overall, this similarity confirms the idea of normal substitutional diffusion of these impurities by the vacancy mechanism in both phases. On the other hand, the diffusion coefficients of Fe, Ni, and Co in β-Ti are about two orders of magnitude higher than the coefficients of Ti self-diffusion [36, 48]. These impurities are known to be fast diffusers also in the z-phase (Section 3.1.1). Although the enhancement rate is not as spectacular as it is in the z-phase, we can assume that the solubility and diffusion of these transition elements in β-Ti have some interstitial component. This assumption was earlier discussed in relation to β-Zr [49], where the diffusion behavior of these impurities is rather similar. As a more specific model, we can suggest the dissociative mechanism, which was initially proposed for metal diffusion in semiconductors [50]. In this model, some part of the impurity atoms dissolves in the matrix material substitutionally and migrates by exchanges with vacancies, while the other part dissolves interstitially and migrates by the direct interstitial mechanism. The dynamic equilibrium between the interstitial (Bi) and substitutional (Bš) configurations of impurity atoms B is maintained by the dissociative reaction

\[ B_i + V_{\text{ann}} \rightarrow B_s, \]  

\[ V \] being a vacancy. The effective diffusion coefficient in this model is not as large as for the direct interstitial mechanism, but it can be significantly larger than for the substitutional diffusion mechanism.

3.1.2.3. Interdiffusion. Interdiffusion in β-Ti(Al) was studied in Ref. [6]. The measurements were performed on single-phase diffusion couples with Al concentrations ranging from zero to almost 40 at.%. In this concentration range, the obtained \( \dot{D} \) values were found to increase with Al concentration by almost an order of magnitude at all diffusion temperatures. Note that this trend stands in contrast with the concentration-independent Ti self-diffusivity found in the same work. The obtained concentration dependencies of \( \dot{D} \) are in good agreement with the earlier work of Ouchi et al. [19], which was limited to lower temperatures and a relatively narrow concentration range (<11 at.% Al). An increase in \( \dot{D} \) values with increasing Al concentration was also observed in earlier measurements on multiphase diffusion couples [17].

An important step taken in Ref. [6] was the evaluation of tracer diffusion coefficients of Al (\( D_{\text{Al}}^\alpha \)) from the known tracer diffusion coefficients of Ti (\( D_{\text{Ti}}^\alpha \)) and the interdiffusion coefficients \( \dot{D} \). This evaluation was based on the Darken–Manning equation [51, 52]

\[ \dot{D} = (c_{\text{Al}} D_{\text{Ti}}^\alpha + c_{\text{Ti}} D_{\text{Al}}^\alpha) \Phi S, \]  

where \( c_{\text{Ti}} \) and \( c_{\text{Al}} \) are the respective atomic fractions in the alloy, and \( \Phi \) is the thermodynamic factor defined as

\[ \Phi = \frac{\partial \ln a_{\text{Ti}}}{\partial \ln c_{\text{Ti}}} = \frac{\partial \ln a_{\text{Al}}}{\partial \ln c_{\text{Al}}}. \]  

Here \( a_{\text{Ti}} \) and \( a_{\text{Al}} \) are the thermodynamic activities of the components in the alloy, \( S \) is the vacancy wind factor introduced by Manning [52]. For a random f.c.c. alloy, Manning’s calculations predict that \( S \) should lie within the limits 1 ≤ \( S \) ≤ 1.28. The thermodynamic factors in the β-phase were determined by Bormann [53] by means of CALPHAD calculations. For example, at 1600 K \( \Phi \) varies between 2 and 2.6 in the concentration range 0.1 < \( c_{\text{Al}} \) < 0.4. The vacancy wind factor was assumed to be \( S = 1 \). At concentrations below 20 at.% Al, the \( D_{\text{Al}}^\alpha \) values determined from equation (4) turned out to be: (i) almost concentration-independent, and (ii) smaller than the respective \( D_{\text{Ti}}^\alpha \) values. The latter relation is well consistent with the results of SIMS measurements of Al impurity diffusion in β-Ti [24]. At larger Al concentrations, however, the \( D_{\text{Al}}^\alpha \) values rapidly increase, and at \( c_{\text{Al}} > 0.25 \) become larger than \( D_{\text{Ti}}^\alpha \).

There were several studies of interdiffusion in single-phase β-Ti(X) diffusion couples, X being an element other than Al. For some elements, like Cr [16, 54] and V [16], \( D \) is almost concentration-independent. In such cases, the interdiffusion profiles are fairly symmetrical, with no detectable shift of inert markers. On the other hand, β-Ti(Mo) couples develop asymmetrical profiles and show a noticeable marker shift. Both the shape of the profiles and the direction of the marker shift indicate that Ti diffusion is faster than Mo diffusion, which is in good agreement with earlier results of direct radio-
tracer measurements [45]. The interdiffusion coefficients in this system decrease with increasing Mo concentration, and remain significantly lower than the coefficients Ti self-diffusion [16].

3.1.3. Diffusion in Al(Ti). Although diffusion in f.c.c.-Al (Ti) lies outside the circle of problems discussed in this article, it is included here for the sake of completeness. Because Al has no suitable isotope for radiotracer or SIMS measurements, self-diffusion in Al has not been measured very accurately. The only two direct studies of Al self-diffusion [55, 56] were carried out using the $^{26}$Al isotope and the mechanical sectioning technique. The Arrhenius parameters are $D_0 = 1.71 \times 10^{-5}$ m$^2$/s and $Q = 1.47$ eV [55]. Other, more indirect measurements (TEM observation of quenched-in voids, nuclear magnetic resonance) typically give smaller activation energies [36]. Diffusion characteristics of several impurities in Al have been determined over the recent years (see Ref. [36] for a summary). The terminal solution Al(Ti) has a very narrow domain of existence (Fig. 1). To our knowledge, Ti diffusion in pure Al or Al(Ti) has never been studied.

3.2. Diffusion in intermetallic compounds

Ti and Al form several intermetallic compounds (Fig. 1). We will focus the discussion on the compounds Ti$_3$Al and TiAl, which are the best studied and the most important technologically. The $\alpha_2$-Ti$_3$Al phase has an ordered h.c.p.-based structure DO$_{19}$ (Fig. 2) which is stable up to 1483 K and has a relatively wide homogeneity range extending from 23 to 35 at.% Al at low temperatures. The $\gamma$-TiAl phase has an ordered f.c.c.-based structure L1$_0$ (Fig. 2) which is even more stable (up to about 1726 K) and has a homogeneity range of 48–55 at.% Al at low temperatures.

3.2.1. Diffusion in Ti$_3$Al

3.2.1.1. Self-diffusion. Ti self-diffusion in Ti$_3$Al has been studied for the first time in our recent work [5]. In that work, the $^{44}$Ti radiotracer and serial sectioning by grinding were applied for diffusion measurements in four alloy compositions: Ti$_{75}$Al$_{25}$, Ti$_{172}$Al$_{28}$, Ti$_{68}$Al$_{12}$ and Ti$_{65}$Al$_{15}$. Because the measurements were made on polycrystalline samples, the penetration profiles showed relatively long tails caused by grain boundary diffusion. The volume diffusion coefficients were deduced from the near-surface parts of the profiles after making corrections for the contributions of grain boundary diffusion. The obtained diffusion coefficients (Fig. 10) are almost concentration-independent, although with some tendency to slightly increase with Al concentration at lower temperatures. An Arrhenius fit to the whole set of diffusion coefficients gives $D_0 = 2.24 \times 10^{-5}$ m$^2$/s and $Q = 2.99$ eV. When extrapolated towards lower temperatures, the diffusion coefficients are smaller than those in $\alpha$-Ti (Fig. 11). This result is not unexpected in view of the geometrical restrictions associated with atomic

![Fig. 10. Ti self-diffusion coefficients in the $\alpha_2$-Ti$_3$Al with different compositions [5].](image)

![Fig. 11. Arrhenius diagram of Ti self-diffusion in different phases of the Ti–Al system: $\alpha$-Ti [10], $\beta$-Ti [9], Ti$_3$Al [5] and TiAl [7].](image)
motion in ordered structures. Note that the difference in diffusion coefficients in these two phases is mainly due to a lower pre-exponential factor for diffusion in Ti$_3$Al, while the activation energies practically coincide within the experimental error.

Al self-diffusion coefficients in Ti$_3$Al have never been measured directly. The results of indirect calculations of $D'_{Al}$ from interdiffusion data will be discussed later.

3.2.1.2. Impurity Diffusion. The first measurements of impurity diffusion in Ti$_3$Al have been performed in Ref. [13]. Diffusion of Fe and Ni was studied by the radiotracer serial sectioning method using the isotopes $^{59}$Fe ($\gamma$-radiation) and $^{63}$Ni ($\beta$-radiation), respectively. Diffusion of Nb was studied by in-depth profiling with SIMS. Several polycrystalline or single-crystalline materials with Al contents ranging from 27 to 33 at.% were used in that work. Within this composition range, the diffusion coefficients were found to be independent of the composition within the experimental error. The temperature dependencies of the obtained diffusion coefficients are shown in the Arrhenius diagram in Fig. 12. This diagram demonstrates that Fe and Ni are fast diffusers in Ti$_3$Al, with their diffusion coefficients being more than two (for Fe) or even three (for Ni) orders of magnitude higher than the coefficients of Ti self-diffusion.

It should be recalled that in disordered $z$-Ti the difference between the coefficients of Ti self-diffusion, on one hand, and the coefficients of Fe and Ni impurity diffusion, on the other hand, is as large as 7–8 orders of magnitude. The fact that, in case of Ti$_3$Al, the effect is not as dramatic may indicate that transition-metal impurities dissolve in this compound both interstitially and substitutionally, and diffuse by a combination of the interstitial and substitutional mechanisms. Again, the dissociative model seems to offer a plausible explanation of the diffusion process. There are at least two arguments in favor of this mechanism. First, the effective diffusion coefficients predicted by the dissociative model lie between the coefficients of purely substitutional and purely interstitial diffusion. Assuming that Ti self-diffusion and Fe (or Ni) impurity diffusion in $z$-Ti represent these two extreme cases, the 2–3 orders of magnitude enhancement over Ti self-diffusion (Fig. 12) seems to be consistent with this model. Second, diffusion by the direct interstitial mechanism would probably occur with a relatively small activation energy. In contrast, the observed activation energy of Fe diffusion in Ti$_3$Al ($Q = 2.87$ eV) is close to that of Ti self-diffusion (2.99 eV). For Ni, which is a faster diffuser than Fe, the activation energy is smaller (2.02 eV), but still not small enough for a purely interstitial mechanism. In the dissociative model [50], on the other hand, the effective diffusion coefficient $D$ in so-called interstitial-controlled conditions is given by

$$D = D_i c_i/c_s.$$  

Here $D_i$ is the interstitial diffusion coefficient and $c_i/c_s$ is the ratio of the interstitial and substitutional solubilities of the impurity atoms. This equation applies when (i) the equilibrium vacancy concentration is maintained by vacancy sinks and sources over the diffusion zone, and (ii) the interstitial solubility is relatively small, i.e. $c_i/c_s \ll 1$. Equation (6) shows that (i) $D \ll D_i$, i.e. the diffusion rates do not have to be as great as they are under the interstitial mechanism, and (ii) because $c_i$ and $c_s$ are temperature-dependent, the apparent activation energy does not have to coincide with that of the interstitial mechanism. For example, if the trend towards interstitial solubility increases with temperature, the apparent activation energy of diffusion can be larger than that for a purely interstitial mechanism.

On the other hand, Nb is a slow diffuser in Ti$_3$Al (Fig. 12). It is likely to be a substitutional element and diffuse by the vacancy mechanism. Because Nb atoms are considered to occupy Ti sites in Ti$_3$Al [57, 58], their diffusion is dominated by exchanges with vacancies on the Ti sublattice. More recently, diffusion of gallium in Ti$_3$Al has been measured with the radiotracer $^{69}$Ga [34]. The obtained Arrhenius parameters are $D_0 = 6.33 \times 10^{-13}$ m$^2$/s and $Q = 3.26$ eV. Notably, Ga has a higher activation energy and shows slower diffusion rates than Ti. Note that this diffusion behavior of Ga is in contrast with that in $z$-Ti, where its activation energy is

![Fig. 12. Arrhenius diagram of impurity diffusion of Fe, Ni and Nb in Ti$_3$Al [13]. The data for Ti self-diffusion in Ti$_3$Al [5] are shown for comparison.](image-url)
lower and diffusion coefficients are higher than those of Ti (Fig. 6).

### 3.2.1.3 Interdiffusion

Interdiffusion in Ti₃Al was studied in Ref. [5] using single-phase diffusion couples Ti₇₅Al₂₅/Ti₆₅Al₃₅. The obtained interdiffusion coefficients tend to increase with Al concentration, but this trend is very weak. Some increase in $D$ values with Al content would be consistent with previous investigations of diffusion in multiphase diffusion couples [17]. Taking the interdiffusion coefficients at 30 at.% Al as representative values, they follow an Arrhenius-type temperature dependence with $D_0 = 1.3 \times 10^{-3}$ m²/s and $Q = 3.26$ eV. Sprengel et al. [59] also studied interdiffusion in Ti₃Al using single-phase diffusion couples Ti₇₂.₅Al₂₇.₅/Ti₆₆Al₃₄. Their diffusion coefficients and the deduced Arrhenius parameters are practically identical to those of Ref. [5]. Furthermore, their interdiffusion coefficients did not show any appreciable concentration dependence either. In contrast, the interdiffusion coefficients found earlier by Hirano and Iijima [18] on multiphase diffusion couples strongly varied with composition and were one to two orders of magnitude higher than those measured in Refs [5, 59].

By combining the obtained interdiffusion and Ti self-diffusion coefficients, the tracer diffusion coefficients of Al ($D^*_A l$) were calculated from the Darken–Manning equation (4). The thermodynamic factors for Ti₃Al, required for such calculations, were determined by Bormann [53] by the CALPHAD method. The vacancy wind factor was assumed to be $S = 1$. It should be remembered that equation (4) was originally derived by Manning [52] on the basis of his random-alloy model. It is not clear for now how accurate this equation is as applied to ordered alloys, particularly with the DO₁₉ structure. There is experimental evidence that this equation works well for the B₂–AuZn phase [60]. Furthermore, Belova and Murch [61] have shown theoretically that Manning’s relations are a good approximation for diffusion in ordered B₂-alloys. However, their analysis essentially relies on the assumption that only inter-sublattice jumps are possible in the structure. They emphasize that other ordered structures in which intra-sublattice jumps may also occur (both the DO₁₉ and L₁₀ structures belong to this class) would require extensive additional considerations. Thus, the calculation of $D^*_A l$ values from equation (4) relies on the assumption that this equation is capable of giving reasonably accurate results for the DO₁₉ structure.

The diffusion coefficients of Al determined this way tend to increase with Al concentration (Fig. 13), but this increase is likely to be within the experimental error. By fitting equation (1) to these $D^*_A l$ values, the Arrhenius parameters $D_0 = 2.32 \times 10^{-1}$ m²/s and $Q = 4.08$ eV were found. Notably, the obtained activation energy is more than 1 eV higher than the activation energy of Ti self-diffusion (2.99 eV). Although this large difference in activation energies is partly compensated for by a larger pre-exponential factor of Al diffusion, Al still diffuses in Ti₃Al up to an order of magnitude higher than those measured in Refs [5, 59].
magnitude slower than Ti in the temperature range of experiments (Fig. 14). The relation $D_{Al}^T < D_{Ti}^T$ is in agreement with previous results of marker shift measurements in α-Ti/TiAl diffusion couples [62]. It is also consistent with the so-called Cu$_3$Au-rule [63], which predicts that the minor element B in ordered compounds A$_3$B must be a slower diffuser.

The obtained diffusion data for Al in Ti$_3$Al can be compared with those for Ga [34], which is known to be a substitute element for Al [58]. Although Al and Ga are chemically different, the data for Ga diffusion were determined by direct radiotracer measurements, and are more reliable than the data for Al. The diffusion coefficients of Ga are close to those of Al, but the activation energy of Ga diffusion (3.26 eV) is considerably lower than that of Al diffusion (4.08 eV). As was argued in Ref. [34], the Darken–Manning equation is capable of giving relatively accurate diffusion coefficients of Al, but involves significant errors in the activation energy.

Finally, it should be noted that Al diffuses slower in Ti$_3$Al than in α-Ti (Fig. 15). Like for Ti self-diffusion in these two phases (cf. Fig. 11), this relation reflects the ordering effect on atomic mobility.

3.2.2. Diffusion in TiAl
3.2.2.1. Self-diffusion. The first study of Ti self-diffusion in γ-TiAl was performed by Kroll et al. [3] using $^{44}$Ti with serial sectioning by grinding. A few years later, Sprengel et al. [14] carefully measured interdiffusion in TiAl using single-phase diffusion couples. By combining their interdiffusion coefficients with Ti self-diffusion coefficients of Kroll et al., we made an attempt to calculate Al self-diffusion coefficients from the Darken–Manning equation (4). Although reliable values of the thermodynamic factor [53] were used in our calculations, the Al diffusion coefficients turned out to be negative. This controversy led us to conclude that the data of Kroll et al. needed to be re-measured with better accuracy.

Therefore, in our recent work [7] we performed more accurate measurements of $^{44}$Ti self-diffusion in TiAl over a wide temperature range. In order to verify the reproducibility of the results, the measurements were made in three different TiAl materials with near-stoichiometric compositions, namely, Ti$_{47}$Al$_{53}$, Ti$_{47}$Al$_{53}$ and Ti$_{46}$Al$_{54}$. The first of them was the material studied previously by Kroll et al. The experimental techniques were essentially the same as in Ref. [3], but the pre-diffusion and diffusion anneals were made longer at most temperatures. The longer anneals gave us two advantages: (i) the penetration profiles were deeper and could therefore be measured with greater accuracy, and (ii) the contributions from short-circuit diffusion along grain boundaries and/or dislocations were eliminated, or at least strongly reduced. The
latter was important because the measurements by Kroll et al. were influenced by short-circuit diffusion, which was evidenced by the overall shape of their profiles [3].

The diffusion coefficients determined by the new measurements (Fig. 16) are systematically lower than those reported in Ref. [3], which additionally confirms that the enhancement caused by short-circuit diffusion was now eliminated. The diffusion coefficients are practically the same for all three compositions. The small differences are most likely due to the different impurity contents in the materials, rather than to deviations from stoichiometry [7]. The most striking feature of Fig. 16 is the non-Arrhenius behavior of the diffusion coefficients, with significant upward deviations at higher temperatures. This behavior was overlooked in the previous work [3] because of the larger scatter of the data points. In the low-temperature range ($T < 1473$ K), where the diffusion coefficients do follow the Arrhenius law, the Arrhenius parameters averaged over all three alloys are $D_0 = 1.43 \times 10^{-6} \text{m}^2/\text{s}$ and $Q = 2.59$ eV. Possible reasons of the enhanced Ti diffusivity at high temperatures were discussed in Ref. [7]. In Fig. 11, the obtained diffusion coefficients are compared with those in other phases of the system. It is observed that Ti is more mobile in TiAl than in Ti$_3$Al, but less mobile than in the disordered phases $\alpha$ and $\beta$.

Al self-diffusion coefficients in TiAl were never measured experimentally. The recent calculations of such coefficients from interdiffusion data will be discussed later.

3.2.2.2. Impurity diffusion. Results of radiotracer measurements of impurity diffusion in TiAl are available for Cr [11, 12] and Co [11, 12], and very recently for Ga [34], Nb [64] and Fe [64]. Overall, the impurity diffusion coefficients are close to Ti self-diffusion coefficients within plus-minus an order of magnitude. This behavior can be explained by purely substitutional solubility and vacancy-mediated diffusion of these impurities in TiAl. Measurements by the atom location channeling enhanced microanalysis suggest that Nb occupies Ti sites in TiAl, Fe and Ga occupy Al sites, while the site preference of Cr depends on the Ti/Al ratio [58]. Nb is a slow diffuser in TiAl, as it is in Ti$_3$Al (cf. Fig. 12). Fe diffuses in TiAl faster than Ti, but the difference between the diffusion coefficients is only a factor of 2–3. Moreover, Fe diffusion shows the same type of non-Arrhenius temperature dependence as that for Ti self-diffusion (cf. Fig. 16). Even the transition temperatures and the activation energies in the low-temperature range are close to one another. This behavior suggests that Fe atoms occupy predominantly Ti-sites and diffuse by the same atomic mechanism as Ti.

It should be admitted that this close similarity in the behavior of Fe and Ti atoms in TiAl is astonishing given the fact that Fe atoms show some interstitial solubility and anomalously fast diffusion in other phases of this system. The most striking is the contrast between the behavior of Fe atoms in TiAl and $\alpha$-Ti, in which the diffusion coefficients of Fe differ by as much as 7–8 orders of magnitude. Fundamental reasons for such radically different mechanisms of solubility and diffusion of Fe and other transition-metal elements in different phases of the Ti–Al system are not well understood at present. Some preliminary understanding can be gained from considering chemical environments of octahedral interstices in different phases, assuming that impurity atoms always "want" to be surrounded by Ti rather than Al atoms [65]. For example, the sizes of octahedral cavities in TiAl and Ti$_3$Al are almost identical, while their chemical environments are different. In TiAl, there are two types of octahedral site, which are present in equal amounts. One type of site is surrounded by two Ti and four Al atoms, while the other by two Al atoms and four Ti atoms. Because the number of Ti neighbors is relatively small, especially in the first case, such sites are not favorable for occupation by impurity atoms. In Ti$_3$Al, there are also two types of octahedral site: one type of sites are surrounded by two Al atoms.

![Fig. 17. Arrhenius diagram of self-diffusion and interdiffusion in TiAl.](image)

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and four Ti atoms (like in TiAl), while the other type of sites are surrounded by six Ti atoms (like in χ-Ti). This may explain why interstitial sites in Ti₃Al are more favorable for occupation than in TiAl. The experimental solubilities of carbon and oxygen in Ti₃Al are indeed higher than in TiAl [65]. The different interstitial solubilities of Fe and Ni in these two phases are probably also due to the difference in local chemical environments.

### 3.2.2.3. Interdiffusion.

As was mentioned above, Sprengel et al. [14] have measured interdiffusion in TiAl around the stoichiometry in single-phase couples Ti₃Al₉₀/Ti₆₄Al₅₄ (Fig. 17). Their interdiffusion coefficients, together with Ti self-diffusion coefficients determined in Ref. [7], were used for the calculation of Al tracer diffusion coefficients in TiAl from the Darken–Manning equation (4). The thermodynamic factors involved in this equation were determined by Bormann [53] by CALPHAD calculations in the framework of the sublattice model. The vacancy wind factor was assumed to be $S = 1.14$. The values of $D_0$ deduced from equation (4) follow, within the scatter of the data points, the Arrhenius relation with $D_0 = 2.11 \times 10^{-2} \text{ m}^2/\text{s}$ and $Q = 3.71 \text{ eV}$.

Al diffusion was also evaluated by using Ga as a substitute for Al. Diffusion of Ga in TiAl was measured by the radiotracer method [34], and the obtained Arrhenius parameters ($D_0 = 4.4 \times 10^{-5} \text{ m}^2/\text{s}$ and $Q = 3.04 \text{ eV}$) were found to be essentially different from those of Al. However, the diffusion coefficients of Ga and Al are remarkably close to one another over a wide temperature range. Overall, there is a trend of Ga diffusivity to become closer to Al diffusivity, and for both to become closer to Ti diffusivity, as we go from χ-Ti to Ti₃Al and then to TiAl. Experimental data confirm that Ga occupies Al sites in both Ti₃Al and TiAl [58]. It was suggested that both Al and Ga diffuse in Ti₃Al and TiAl via anti-structural defects on the Ti-sublattice [34].

The Arrhenius diagram in Fig. 15 summarizes the

<table>
<thead>
<tr>
<th>Diffuser</th>
<th>Matrix</th>
<th>$D_0$ (m²/s)</th>
<th>$Q$ (eV)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>χ-Ti</td>
<td>1.35 × 10⁻³</td>
<td>3.14</td>
<td>R</td>
<td>[10]</td>
</tr>
<tr>
<td>Ti</td>
<td>β-Ti</td>
<td>3.53 × 10⁻⁶</td>
<td>3.40</td>
<td>R</td>
<td>[9]</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti₃Al</td>
<td>2.24 × 10⁻⁵</td>
<td>2.99</td>
<td>R</td>
<td>[5]</td>
</tr>
<tr>
<td>Ti</td>
<td>Ti₃Al</td>
<td>1.43 × 10⁻⁶</td>
<td>2.59</td>
<td>R</td>
<td>[7]</td>
</tr>
<tr>
<td>Al</td>
<td>χ-Ti</td>
<td>6.69 × 10⁻³</td>
<td>3.41</td>
<td>SIMS</td>
<td>[10]</td>
</tr>
<tr>
<td>Al</td>
<td>β-Ti</td>
<td>1.94 × 10⁻⁴</td>
<td>3.36</td>
<td>SIMS</td>
<td>[24]</td>
</tr>
<tr>
<td>Al</td>
<td>Ti₃Al</td>
<td>2.32 × 10⁻⁴</td>
<td>4.08</td>
<td>DM</td>
<td>[5]</td>
</tr>
<tr>
<td>Al</td>
<td>Ti₃Al</td>
<td>2.11 × 10⁻²</td>
<td>3.71</td>
<td>DM</td>
<td>[7]</td>
</tr>
</tbody>
</table>

| $a$ = $\frac{n}{n + m}$, $b = \frac{m}{n + m}$, (7) |

where $a + b = 1$. Under real conditions the compound may have a non-stoichiometric composition $A_{x+s}B_{1-x}$, where parameter $x$ measures the devi-
ation from stoichiometry. The atomic fractions of components A and B are given by

\[ c_A = a + x, \quad c_B = b - x, \quad \text{(8)} \]

with \( c_A + c_B = 1 \). In most theoretical models of atomic disorder the off-stoichiometry is assumed to be small: \( |x| \ll 1 \).

We assume that the structure of the compound consists of two sublattices, denoted here as \( \alpha \) and \( \beta \). In a stoichiometric compound at zero temperature these sublattices are occupied by atoms A and B, respectively. As a stoichiometric compound is heated up, it becomes partly disordered (thermal disorder). We assume that thermal disorder occurs by a generation of the following four types of point defects:

\[
\begin{align*}
V_\alpha &= \text{vacancy on sublattice } \alpha \\
V_\beta &= \text{vacancy on sublattice } \beta \\
B_\alpha &= \text{antisite defect on sublattice } \alpha \\
A_\beta &= \text{antisite defect on sublattice } \beta.
\end{align*}
\]

These defects can be viewed as elementary thermal excitations of a perfect crystal. They obviously appear in amounts that conserve the alloy composition.

The same four types of point defect accommodate deviations of the alloy composition from ideal stoichiometry (compositional disorder). For example, deviations towards B-rich compositions can be accommodated by extra antisites \( B_\alpha \) and/or vacancies \( V_\alpha \). The extra defects which accommodate off-stoichiometry are called constitutional defects. At low temperatures all thermal defects are "frozen out" and atomic disorder is dominated by constitutional defects, whose concentration is determined exclusively by the deviation from stoichiometry. For any given off-stoichiometric composition, there is only one type of constitutional defect: the one which has the lowest energy at \( T \rightarrow 0 \). Importantly, constitutional defects can be the same or different on either side of the stoichiometry. In so-called triple-defect compounds (e.g. NiAl or CoGa) the constitutional defects are \( A_\beta \)-antisites in A-rich compositions and \( V_\beta \)-vacancies in B-rich compositions [66]. In contrast, in antisite-disorder compounds the constitutional defects are \( A_\alpha \)-antisites in A-rich compositions and \( B_\alpha \)-antisites in B-rich compositions. Both Ti₃Al and TiAl belong to anti-site-disorder compounds.

Most theoretical treatments describe atomic disorder in compounds in terms of a "gas" of non-interacting point defects [67]. This model is only valid as long as the concentrations of point defect are small enough to neglect their interactions. This, in turn, is only possible if the compound is strongly ordered and the off-stoichiometry is relatively small. Under such conditions all statistical-mechanical calculations can be limited to the first order in point-defect concentrations. Thus, the energy of the crystal per lattice site can be approximated by

\[ U = U_0 + \sum_P c_P \epsilon_P. \quad \text{(9)} \]

Here the point defect concentrations \( c_P \) (symbol \( P = V_\alpha, V_\beta, B_\alpha, \) or \( A_\beta \) refers to point defect types) are expressed as occupation probabilities per lattice site, \( U_0 \) is the so-called cohesive energy of a perfect stoichiometric crystal per atom, i.e. the energy change due to the formation of a crystal out of isolated atoms divided by the number of atoms. The quantities \( \epsilon_P \) in equation (9) are so-called "raw" energies of point defects at \( T = 0 \), which can be conveniently determined by atomistic computer simulations [68]. By definition, the "raw" energy of a point defect is the total energy change due to the defect formation in an initially perfect crystal with a fixed number of lattice sites. For example, a vacancy is created by taking an atom out of the system, while an antisite is created by changing the chemical sort of an atom. The total energy of the simulation block is determined by static relaxation at zero temperature and pressure. This relaxation includes not only local atomic displacements but also variations of the block volume during the energy minimization. As was explained elsewhere [68], the "raw" energy of a defect is not a useful quantity by itself and should not be confused with the point-defect formation energy defined in statistical mechanics of solids. The latter is determined while keeping the numbers of all atoms in the system fixed. In contrast, the formation of a point defect in a manner just described obviously changes such numbers. Nevertheless, the full set of "raw" energies \{\( \epsilon_P \)\} together with \( U_0 \) forms the input data set for the model which will be used below for the calculation of the equilibrium defect concentrations \{\( c_P \)\}.

The configurational entropy of the point-defect subsystem per lattice site can be conveniently written down as

\[
S/k_B = -\sum_P c_P \ln X_P - aX_{A_\alpha} \ln X_{A_\alpha} - bX_{B_\alpha} \ln X_{B_\alpha},
\]

where \( X_P \) are site concentrations of point defects relative to their sublattices. These are related to \( c_P \) concentrations as

\[
\begin{align*}
\text{c}_{V_\alpha} &= aX_{V_\alpha}, \\
\text{c}_{V_\beta} &= bX_{V_\beta}, \\
\text{c}_{B_\alpha} &= aX_{B_\alpha}, \\
\text{c}_{A_\beta} &= bX_{A_\beta},
\end{align*}
\]

We have also introduced the atomic concentrations, \( X_{A_\alpha} \) and \( X_{B_\alpha} \), on the respective sublattices.

Assuming zero external pressure, the Gibbs free energy per lattice site can be constructed from
equations (9) and (10) as

$$G = U - TS. \quad (12)$$

Equations (9)-(12) represent a simple statistical model of point defect disorder in a compound. This model can be further refined by including other effects, such as (1) entropy contributions, $s_P$, associated with other, non-configurational degrees of freedom, e.g. with atomic vibrations, or (2) point defect formation volumes, which are essential if we want to include the pressure effect. For example, atomic vibrations can be conveniently included in the quasi-harmonic model. In the first approximation, we can retain the structure of equations (9) and (10), but the energies $\epsilon_P$ will be replaced by the Gibbs free energies

$$g_P = \epsilon_P - T s_P + p \Omega_P. \quad (13)$$

Here the “raw” point-defect entropies $s_P$ and volumes $\Omega_P$ are calculated by the same scheme as the “raw” energies $\epsilon_P$, namely from molecular statistics at $T = 0$ and $p = 0$ with a fixed number of lattice sites. Obviously, the volumes $\Omega_P$ determined by this scheme have the meaning of relaxation volumes of defect formation. The cohesive energy $\epsilon_0$ will be also replaced by

$$g_0 = \epsilon_0 - T s_0 + p \Omega_0. \quad (14)$$

$s_0$ and $\Omega_0$ being the non-configurational entropy per atom and the average atomic volume of the perfect crystal, respectively. Note that including the last terms in the right-hand sides of equations (13) and (14) is equivalent to adding the usual $p \Omega$ term ($\Omega$ being the average volume per crystal site) to equation (12) [69]. In effect, equations (13) and (14) approximate $\Omega$ by an additive expression

$$\Omega = \Omega_0 + \sum_P \epsilon_P \Omega_P. \quad (15)$$

This approximation is based on the intuitive idea that volume effects associated with defect formation are distributed uniformly over the crystal [69]. The same kind of additivity is assumed for the total non-configurational entropy of the crystal.

The above equations can be applied for the calculation of equilibrium point defect concentrations. There can be different ways of performing such calculations, which of course must give identical results if applied properly. Some workers [70–76] used the grand canonical ensemble formalism, which directly involves the chemical potentials of the species, $\mu_A$ and $\mu_B$. In this method, the total number of lattice sites $N$ is fixed and the grand potential $\Psi = NG - N_A \mu_A - N_B \mu_B$ ($N_A$ and $N_B$ being numbers of A and B atoms in the system) is minimized subject to appropriate constraints. From this minimization, the point defect concentrations and the equilibrium values of $N_A$ and $N_B$ (and thus the alloy composition) are determined as functions of temperature and the chemical potentials. An alternative way is to apply the canonical ensemble method [66, 67, 69, 77–80]. In this case it is $N_A$ and $N_B$ that are fixed, while the number of lattice sites can vary. The Gibbs free energy $N \epsilon$ is then minimized with respect to point defect concentrations subject to one constraint that maintains the atomic balance in the system:

$$x(1 - aX_{V_A} - bX_{V_B}) = bX_{A_p} - aX_{B_m} + ab(X_{V_A} - X_{V_B}). \quad (16)$$

The off-stoichiometry parameter $x$, defined by equation (8), must be fixed during the minimization. This constraint can be included in the minimization procedure via a Lagrange multiplier. Neglecting quadratic and higher order terms in point-defect concentrations, equation (16) can be written as

$$x = bX_{A_p} - aX_{B_m} + ab(X_{V_A} - X_{V_B}). \quad (17)$$

Although the chemical potentials are not a part of this calculation scheme, they can be determined separately if necessary [69].

In what follows we will introduce yet another possible approach to point-defect calculations in compounds. Although it gives precisely the same results as the previous two, the calculation procedure is more illustrative and transparent. Namely, we can write dynamic equilibrium conditions for three independent “chemical” reactions in the four-component “gas” of point defects. Each equilibrium condition will have the form of a mass action law. The four unknown point defect concentrations can be determined from these equilibrium conditions complemented with the atomic balance equation (17). Although any set of three independent reactions must lead to the same result, we can always choose the most convenient reactions based on a priori knowledge, or guess, of the disorder mechanism in the compound. For antisite-disorder compounds the following set of defect reactions provides a suitable choice:

$$(n + m) V_\alpha + A_n B_m = m B_\alpha \quad (18)$$

$$(n + m) V_\beta + A_n B_m = n A_\beta \quad (19)$$

$$B_\alpha + A_\beta \rightarrow \text{eq} \rightarrow 0. \quad (20)$$

In reaction (18), we fill $n + m$ vacancies on sublattice $z$ with one formula unit $A_n B_m$. The $n$ atoms A will eliminate $n$ vacancies, while the $m$ atoms B will turn the remaining $m$ vacancies into antisite defects $B_\alpha$. Reaction (19) has a similar meaning with the vacancies on sublattice $\beta$. Reaction (20) creates or eliminates a pair of antisites by exchanging two atoms A and B.
In order to describe the dynamic equilibrium with respect to these reactions, we formally assign the chemical potentials

\[ \mu_{V_i} = \epsilon_{V_i} + k_B T \ln(X_{V_i}/X_{A_i}) \]

\[ \mu_{V_j} = \epsilon_{V_j} + k_B T \ln(X_{V_j}/X_{B_j}) \]

\[ \mu_{B_i} = \epsilon_{B_i} + k_B T \ln(X_{B_i}/X_{A_i}) \]

\[ \mu_{A_j} = \epsilon_{A_j} + k_B T \ln(X_{A_j}/X_{B_j}) \]

(21)

to the point defects involved in the reactions. We also assign the chemical potential

\[ \mu_{A_nB_m} = (n+m)\epsilon_0 + k_B T n \ln X_{A_n} + k_B T m \ln X_{B_m} \]

(22)
to a formula unit \( A_nB_m \) of the compound. The assignment of chemical potentials to point defects reflects the idea that they can be treated as a gas of elementary excitations, or “quasi-particles”, in the initially perfect crystal. Note that equations (21) and (22) are consistent with the thermodynamic definition of a chemical potential, on one hand, and with equations (9)–(12) for the Gibbs free energy \( G \), on the other hand. In particular, the Gibbs free energy of a defected crystal per lattice site can be represented as

\[ G = \mu_{A_nB_m} / (n+m) + \sum \epsilon_p \mu_p. \]

(23)
The dynamic equilibrium conditions are obtained by replacing the symbols of the “chemical species” in reactions (18)–(20) by the respective chemical potentials. This immediately gives

\[ k_B T \ln \frac{X_{V_i}}{X_{A_i}}^b = \beta_{B_i} - \epsilon_{V_i} - \epsilon_0 \]

(24)

\[ k_B T \ln \frac{X_{V_j}}{X_{B_j}}^a = \alpha_{A_j} - \epsilon_{V_j} - \epsilon_0 \]

(25)

\[ k_B T \ln \frac{X_{B_i}}{X_{A_i}}^a = -\epsilon_{B_i} - \epsilon_{A_j} \]

(26)

Because the underlying model is based on the assumption of small point defect concentrations, the above equations can be simplified by replacing \( X_{A_i} \) and \( X_{B_j} \) by unity. This gives:

\[ k_B T \ln \frac{X_{V_i}}{X_{B_i}}^b = \beta_{B_i} - \epsilon_{V_i} - \epsilon_0 \]

(27)

\[ k_B T \ln \frac{X_{V_j}}{X_{B_j}}^a = \alpha_{A_j} - \epsilon_{V_j} - \epsilon_0 \]

(28)

\[ k_B T \ln \frac{X_{B_i}}{X_{A_i}}^a = -\epsilon_{B_i} - \epsilon_{A_j} \]

(29)

We note that the same equations could be obtained by putting \( X_{A_i} = X_{B_j} = 1 \) already in equations (21) and (22), which would simplify them to

\[ \mu_p = \epsilon_p + k_B T \ln X_p \]

(30)

\[ \mu_{A_nB_m} = (n+m)\epsilon_0. \]

(31)

These two equations provide a practical definition of chemical potentials in the quasi-chemical methods described here.

Equations (27)–(29) together with equation (17) can be solved for four unknowns \( X_p \) by numerical methods, for example by the iterative procedure described below. The site concentrations \( c_p \) can be then calculated from equation (11) if necessary. That way the equilibrium point defect concentrations can be found as functions of temperature and composition around the stoichiometry.

In practice, the “raw” energies of individual point defects are usually calculated using a lattice block with periodic boundary conditions (supercell). Such calculations involve an important issue of reference energies, which was discussed in depth by Hagen and Finnis [69]. Because the creation of a defect destroys the stoichiometry of the block, the “raw” energies depend on the reference energies of constituent atoms. If the calculations are performed with semi-empirical pair potentials or embedded-atom potentials, the energy of an isolated atom is conventionally assumed to be zero regardless of its chemical sort. The energy of a simulation block is then defined relative to the reference state in which all atoms of the block are isolated. This choice of reference energies is not unique, and in particular it does not apply in first-principles calculations. Therefore, the “raw” energies of point defects determined by first-principles methods are essentially different from those obtained with semi-empirical potentials. Nevertheless, the combinations appearing in the right-hand sides of equations (27)–(29) do not depend on the arbitrary choice of reference energies. Indeed, arbitrary changes in the reference energies of atoms A and B by amounts \( \epsilon_A \) and \( \epsilon_B \), respectively, would result in the following transformations of the “raw” energies \( \epsilon_p \) and the cohesive energy \( \epsilon_0 \):

\[ \epsilon_{V_i} \rightarrow \epsilon_{V_i} - \epsilon_A \]

(32)

\[ \epsilon_{V_j} \rightarrow \epsilon_{V_j} - \epsilon_B \]

(33)

\[ \epsilon_{B_i} \rightarrow \epsilon_{B_i} + \epsilon_B - \epsilon_A \]

(34)


\[ \epsilon_{A_0} \rightarrow \epsilon_A + \epsilon_A - \epsilon_B \]  
\[ \epsilon_0 \rightarrow \epsilon_0 + a\epsilon_A + b\epsilon_B. \]  

One can verify by substitution that the right-hand sides of equations (27)–(29) are invariant under these transformations. Thus, the reference energies have no effect on the point defect concentrations determined from equations (27)–(29). These equations are, therefore, equally suitable for both semi-empirical and first-principles methods of calculation.

Knowing the temperature dependencies of \( X_P \), we can determine the so-called “effective” formation energies of the defects. By definition, if \( X_P \) depends on temperature according to an Arrhenius-type relation

\[ X_P = X_P^0 \exp(-E^t_P/k_B T), \]  
then \( E^t_P \)’s is called the effective formation energy of defect P. Although equation (37) does not have to be followed exactly, in many practical cases it provides a good approximation of functions \( X_P(T) \) over a wide temperature range. Note that the effective formation energies may depend on the alloy composition. As will be shown later, they play an important role in diffusion calculations. They also provide a basis of comparison with experiments, where point defect formation energies are traditionally determined by approximating the measured point defect concentrations with equation (37).

It is useful to derive analytical expressions for \( E^t_P \)’s in a few important limiting cases. Bearing the compounds Ti₃Al and TiAl in mind, we will consider a generic antisite-disorder compound \( A_bB_m \). Because in such compounds the antisite defect concentrations are much greater than the vacancy concentrations, the atomic-balance equation (17) can be simplified to

\[ x = bX_{A_b} - aX_{B_m}. \]  

By combining this equation with equation (29) we get a quadratic equation, which is immediately solved for the antisite defect concentrations:

\[ X_{A_b} = -x/2a + \left( \frac{x^2}{4a^2} + \frac{bK}{a} \right)^{1/2}, \]  
\[ X_{B_m} = \frac{x}{2b} \left( \frac{x^2}{4b^2} + \frac{aK}{b} \right)^{1/2}, \]  
where

\[ K = \exp \left( -\frac{\epsilon_{B_m} + \epsilon_{A_b}}{k_B T} \right). \]  

These concentrations known, we can determine the vacancy concentrations from equations (27) and (28):

\[ X_{V_b} = X_{B_m}^{h \beta} \exp \left( -\frac{\epsilon_{V_b} + \epsilon_0 - b\epsilon_{B_m}}{k_B T} \right) \]  
\[ X_{V_m} = X_{A_b}^{a \beta} \exp \left( -\frac{\epsilon_{V_m} + \epsilon_0 - a\epsilon_{A_b}}{k_B T} \right). \]  

Equations (39)–(43) can be further simplified by considering three limiting cases depending on the alloy composition:

1. **Stoichiometric compound** \((x = 0)\). The atomic balance equation (38) becomes

\[ bX_{A_b} = aX_{B_m}, \]  

while equations (39) and (40) give

\[ X_{B_m} = \left( \frac{b}{a} \right) \left( \frac{\epsilon_{B_m} + \epsilon_{A_b}}{2k_B T} \right)^{1/2} \]  
\[ X_{A_b} = \left( \frac{a}{b} \right) \left( \frac{\epsilon_{B_m} + \epsilon_{A_b}}{2k_B T} \right)^{1/2}. \]  

A substitution of these expressions in equations (42) and (43) gives the vacancy concentrations:

\[ X_{V_b} = \left( \frac{b}{a} \right)^{h \beta} \exp \left( -\frac{b\epsilon_{A_b} - 2\epsilon_{V_b} + 2\epsilon_0}{2k_B T} \right) \]  
\[ X_{V_m} = \left( \frac{a}{b} \right)^{a \beta} \exp \left( -\frac{a\epsilon_{B_m} - 2\epsilon_{V_m} + 2\epsilon_0}{2k_B T} \right). \]  

2. **A-rich compound** \((x > 0)\). Because the surplus atoms A go to sublattice B to form anti-structural defects \( A_B \), the term \( bX_{A_b} \) in equation (38) strongly dominates over \( aX_{B_m} \). We therefore have

\[ X_{A_b} = x/b. \]  

Thus, in this limit the concentration of antisites \( A_B \) does not depend on temperature and is solely determined by the alloy composition. By replacing \( X_{A_b} \) in equation (29) by expression (49) we find

\[ X_{B_m} = \frac{x}{b} \exp \left( -\frac{\epsilon_{B_m} + \epsilon_{A_b}}{k_B T} \right). \]  

For the vacancy concentrations determined from equations (42) and (43) we have

\[ X_{V_b} = \left( \frac{b}{x} \right)^{h \beta} \exp \left( -\frac{\epsilon_{V_b} + \epsilon_0 + b\epsilon_{A_b}}{k_B T} \right) \]  
\[ X_{V_m} = \left( \frac{b}{x} \right)^{a \beta} \exp \left( -\frac{\epsilon_{V_m} + \epsilon_0 + a\epsilon_{A_b}}{k_B T} \right). \]
Table 3. Analytical expressions for effective formation energies of point defects in an antisite-disorder compound $A_{b}B_{m}c_{P}(P-V_{a}, V_{b}, B_{m}$ or $A_{b})$ are “raw” energies of the point defects $P$. The stoichiometry factors $a$ and $b$ are given by equation (7).

<table>
<thead>
<tr>
<th>B-rich alloy</th>
<th>Stoichiometric alloy</th>
<th>A-rich alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{a}$</td>
<td>$\epsilon_{V_{a}} + \epsilon_{B_{b}} - b\epsilon_{a_{b}}$</td>
<td>$\epsilon_{V_{a}} + \epsilon_{B_{b}} - b\epsilon_{a_{b}}$</td>
</tr>
<tr>
<td>$V_{b}$</td>
<td>$\epsilon_{V_{b}} - b\epsilon_{a_{b}}$</td>
<td>$\epsilon_{V_{b}} + \epsilon_{B_{b}} + b\epsilon_{a_{b}}$</td>
</tr>
<tr>
<td>$A_{b}$</td>
<td>$\epsilon_{a_{b}} + \epsilon_{B_{b}}$</td>
<td>$\epsilon_{B_{b}} + a\epsilon_{b}$</td>
</tr>
</tbody>
</table>

\[
X_{V_{b}} = \left(\frac{X}{b}\right)^{a} \exp\left(-\frac{\epsilon_{V_{b}} + \epsilon_{B_{b}} - a\epsilon_{a_{b}}}{k_{B}T}\right). \tag{52}
\]

(3) B-rich compound ($x < 0$). In this case the surplus atoms $B$ go to sublattice $x$ to form anti-structural defects $B_{x}$. Accordingly, the term $bX_{A_{b}}$ in equation (38) can be neglected and this equation becomes

\[
X_{B_{x}} = -\frac{\epsilon_{a_{b}}}{a}. \tag{53}
\]

Again, the concentration of antisites $B_{x}$ is temperature-independent and is solely determined by the alloy composition. By combining equations (29) and (53) we obtain

\[
X_{A_{b}} = \frac{\epsilon_{a_{b}}}{a} \exp\left(-\frac{\epsilon_{B_{b}} + \epsilon_{a_{b}}}{k_{B}T}\right). \tag{54}
\]

The vacancy concentrations determined from equations (42) and (43) are given by

\[
X_{V_{a}} = \left(\frac{x}{a}\right)^{b} \exp\left(-\frac{\epsilon_{V_{a}} + \epsilon_{B_{b}}}{k_{B}T}\right). \tag{55}
\]

\[
X_{V_{b}} = \left(\frac{a}{x}\right)^{a} \exp\left(-\frac{\epsilon_{V_{b}} + \epsilon_{B_{b}} + a\epsilon_{a_{b}}}{k_{B}T}\right). \tag{56}
\]

Note that the obtained expressions for point defect concentration satisfy the Arrhenius form (25). The formulae for the effective formation energies of point defects, deduced from the above expressions, are summarized in Table 3. Like the basic equations (27)–(29), these formulae are invariant with respect to transformations (32)–(36). Therefore, the obtained effective formation energies do not depend on reference energies of the elements and can be calculated with either semi-empirical potentials or first-principles methods. For the special case of TiAl ($a = b = 0.5$), identical expressions were derived, although in a different way, by Woodward et al. [76]. Those authors used these expressions in conjunction with first principles calculations.

Generally, both constitutional and thermal defects are present in a compound. While the concentration of constitutional defects is temperature-independent and is determined by the alloy composition only, the concentration of thermal defects of any given type normally obeys the Arrhenius law (37).† This law is, therefore, followed exactly only in limiting cases in which the atomic disorder is dominated by either thermal or constitutional defects. In the latter case we formally have $E_{f_{p}}^{P} = 0$. In intermediate regimes, the point defect concentrations can be better described by a sum of an Arrhenius exponent and a constant. In such intermediate cases the defect concentrations may show some upward curvature when plotted in Arrhenius coordinates log $c_{P}$ vs $1/T$.

We note also that zero effective formation energies of constitutional defects (Table 3) are consistent with the definition of such defects. All other $E_{f_{p}}^{P}$ values relate to thermal defects and must be positive. A negative $E_{f_{p}}^{P}$ value would mean that the defect does not disappear at low temperatures, which in turn would indicate that constitutional defects in the compound were misidentified.

Returning to equations (27)–(29), for an antisite-disorder compound they can be solved numerically by the following iterative procedure. At each step, we calculate $X_{B_{x}}$ and $X_{A_{b}}$ by solving the double-antisite equation (29) simultaneously with the atomic-balance equation (17), using the vacancy concentrations obtained from the previous iteration. This essentially reduces to solving a quadratic equation. The new antisite-defect concentrations are then substituted in equations (27) and (28) to obtain updated values of the vacancy concentrations. After that we proceed to the next iteration and continue to self-consistency. In fact, the expressions for the effective formation energies listed in Table 3 were derived by implementing one such iteration analytically assuming $X_{V_{a}} = X_{V_{b}} = 0$ as the initial guess.

Similarly to equation (37), we can define the effective formation volume of defect $P$, $\Omega_{f_{p}}$, through an exponential pressure dependence of concentration $X_{P}$:

\[
X_{P} = X_{P}^{0} \exp(-\rho\Omega_{f_{p}}/k_{B}T). \tag{57}
\]

Here the pre-exponential factor is different from that in equation (37). The effective formation volumes can be easily determined in the limiting cases considered above.

Indeed, we saw that in such cases the effective formation energies $E_{f_{p}}^{P}$ were linear combinations of the “raw” energies and $\epsilon_{0}$:

\[
E_{f_{p}}^{P} = \lambda_{0}\epsilon_{0} + \sum_{P} \lambda_{PP'}\epsilon_{P'}. \tag{58}
\]
Here the coefficients $\lambda_{p0}$ and $\lambda_{pp'}$ depend on the stoichiometry factors only (Table 3). It was also pointed out that the non-configurational entropy and the volume effects can be included by replacing $\epsilon_p$ and $\epsilon_0$ by expressions (13) and (14), respectively. Then, the Arrhenius relation (37) takes a generalised form

$$X_p = X_p^0 \exp(-G_p^f/k_BT),$$

where $G_p^f$ is the effective Gibbs free energy of defect formation. By virtue of equation (58), $G_p^f$ equals

$$G_p^f = \lambda_{p0}\epsilon_0 + \sum_{p'}\lambda_{pp'}\epsilon_{p'},$$

from which it follows that

$$\Omega_p^f = \lambda_{p0}\Omega_0 + \sum_{p'}\lambda_{pp'}\Omega_{p'}.$$  

Thus, similarly to the effective formation energy, the effective formation volume of defect P depends linearly on the relaxation volumes of all point defects present in the crystal. It follows also that the effective formation entropy of defect P equals

$$S_p^f = \lambda_{p0}\epsilon_0 + \sum_{p'}\lambda_{pp'}s_{p'}.$$  

Taking this entropy into account, the pre-exponential factor in expression (37) for a defect concentration at zero pressure becomes $X_p^0 \exp(S_p^f/k_BT)$. Here $X_p^0$ depends on the stoichiometry factor only.

Finally, we want to make a practical comment on calculating the vibrational entropy of point defect formation. In the harmonic approximation, the vibrational entropy of a periodic N-atomic block equals

$$S = -k_B \sum_{i=1}^{3N-3} \ln \frac{\hbar v_i}{k_BT} + (3N-3)k_B,$$

$v_i$ being the frequencies of normal vibrations, $\hbar$ the Planck constant. This expression takes into account that three eigenvalues of the dynamic matrix, out of $3N$, are zero due to translational invariance of the total energy. Since the formation of an antisite does not change the number of atoms in the block, the “raw” entropy of an antisite can be calculated as

$$s_p = -k_B \ln \frac{\prod_{i=1}^{3N-3} v_i}{\prod_{i=1}^{3N-3} v_i^0},$$

$v_i^0$ being normal vibrations of a perfect-lattice block, $P = \alpha$ or $\beta$. Because the initial and final states have the same number of degrees of freedom, the second term in equation (63) and the factor $k_BT$ cancel out. The case of a vacancy must be treated separately. Namely, it follows from equation (62) and Table 3 that in any expression for $S_p^f$ “raw” vacancy entropy $s_p$ necessarily appears as a sum with the perfect-lattice entropy $s_0$. This sum represents the entropy change of an ($N - 1$)-atomic block and can be calculated as

$$s_p + s_0 = -k_B \ln \frac{\prod_{i=1}^{3N-6} v_i}{\prod_{i=1}^{3N-6} v_i^0},$$

where $P = V_\alpha$ or $V_\beta$. In calculations with fixed boundary conditions all eigenvalues of the dynamic matrix are positive, and equations (64) and (65) should be modified accordingly.

### 4.2. Results for Ti$_3$Al and TiAl

Having this background we can now turn to specific calculations for Ti$_3$Al and TiAl. They were carried out by zero-pressure molecular statics with embedded-atom potentials [84]. The calculations for Ti$_3$Al were performed in this paper, while those for TiAl were published previously [7]. In both cases the simulation block contained around 1400 atoms with periodic boundary conditions. Effects of atomic vibrations and thermal expansion were neglected. The obtained “raw” energies of point defects are listed in Table 4. Using these energies, the equilibrium point defect concentrations were calculated by numerical solution of equations (27)–(29) and (17) using the iterative procedure described in Section 4.1.

Figure 18 illustrates the obtained point defect concentrations as functions of composition at $T = 1200$ K. Note that the calculated compositions ranges are somewhat wider than the actual homogeneity ranges of the compounds (cf. Fig. 1). In both compounds, antisites strongly dominate over vacancies at all temperatures and compositions, which confirms that Ti$_3$Al and TiAl are antisite-disorder compounds. This conclusion is consistent with previous experimental studies [85–88] and Bragg–Williams model calculations [89, 90], as well as with recent first-principles calculations for TiAl [71, 76, 91]. Importantly, in both compounds there

<table>
<thead>
<tr>
<th>Ti$_3$Al</th>
<th>V$_{Ti}$</th>
<th>V$_{Al}$</th>
<th>Al$_{Ti}$</th>
<th>Ti$_{Al}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$Al</td>
<td>-4.674</td>
<td>6.214</td>
<td>5.801</td>
<td>1.216</td>
</tr>
<tr>
<td>TiAl</td>
<td>-4.396</td>
<td>6.257</td>
<td>5.092</td>
<td>1.859</td>
</tr>
</tbody>
</table>
are always more Ti-vacancies than Al-vacancies, especially in Al-rich compositions. This was also predicted by earlier calculations within the Bragg–Williams model (for Ti3Al [89] and TiAl [90]) and by first-principles methods (for TiAl [71, 76, 91]). Note also that the concentration of Ti vacancies in Ti3Al shows a much weaker composition dependence than in TiAl.

In Fig. 19 we show temperature dependencies of Ti vacancy concentrations in Ti3Al and TiAl for selected compositions. It is seen that the Arrhenius relation (37) is indeed followed very accurately in a wide temperature range. Arrhenius diagrams of Al vacancy concentration are not shown here, but they also demonstrate a linear behavior. Arrhenius plots for antisite-defect concentrations reveal some curvature in off-stoichiometric compositions in which the respective antisites are constitutional defects. This curvature arises from the contribution of constitutional defects to the overall defect concentration.

The effective formation energies of point defects were determined by approximating the defect concentrations by equation (37) in the temperature range 1200–1400 K. The obtained \( E_f \) values are plotted as functions of composition in Fig. 20. As expected from the antisite disorder model, vacancies have higher formation energies than antisites in both compounds, this difference being larger in Ti3Al. The defect formation energies are more sensitive affected by the alloy composition in TiAl than in Ti3Al. Ti vacancies form more easily than Al vacancies, which is consistent with their higher concentrations (cf. Fig. 18). The relation \( E_{VTi} < E_{VAl} \) reverses only at \( c_{Ti} > 0.52 \) in TiAl, but such compositions exceed the solubility limit of Ti in TiAl. The relation \( E_{VTi} < E_{VAl} \) was also predicted by earlier nearest-neighbor bond model calculations for Ti3Al [89] and TiAl [90]. Recent experimental measurements by positron lifetime spectroscopy gave 1.55 ± 0.2 and 1.41 ± 0.06 eV for vacancy formation energies in Ti71Al23 [89] and Ti52Al48 [87, 88], respectively. These values are in reasonable agreement with our results for these compositions, namely, \( E_{VTi} = 1.34 \) eV in Ti3Al and \( E_{VAl} = 1.28 \) eV in TiAl. We note also that antisite-defect formation energies are higher in TiAl than in Ti3Al (e.g. 0.442 vs 0.313 eV at stoichiometry). The stronger ordering trend in TiAl correlates with its higher ordering temperature (see Fig. 1).

The effective formation energies of point defects vary most rapidly near stoichiometry and show a saturation tendency as off-stoichiometry increases (Fig. 20). The saturation levels represent the limiting cases which were analyzed in Section 4.1. Table
5 summarizes the defect formation energies in such limiting cases. They were calculated using the analytical expressions given in Table 3 and the "raw" energies listed in Table 4. For TiAl, the obtained formation energies show the same trends as those calculated from first principles [76], although the energies obtained by the embedded-atom method are consistently lower.

For further comparison between first-principles and embedded-atom calculations, we can examine the energies of four composition-conserving point-defect complexes in TiAl, namely a divacancy $V_{Ti} + V_{Al}$, a double antisite $Al_{Ti} + Ti_{Al}$, and triple defects $2V_{Ti} + Ti_{Al}$ and $2V_{Al} + Al_{Ti}$. The point defects involved in these complexes are treated as isolated. Analytical expressions for the complex energies [68, 76] are given in Table 6. These expressions are invariant under transformations (32)–(36), which could be expected from the conservation of chemical composition by such complexes. The energies of these complexes can be, therefore, used as a basis for comparison between different methods of calculation. Woodward et al. [76] computed these energies using a plane-wave pseudopotential method. Their complex energies are consistently higher than those predicted by the embedded-atom method (Table 6). This discrepancy could arise from two sources: on one hand, because of the limited size of the supercell and incomplete relaxation the first-principles calculations [76] might overestimate the defect formation energies. On the other hand, the employed embedded-atom potentials could not be well optimized, not to mention the inherent limitations of the embedded-atom model, especially as applied to TiAl in which directional bonding can be significant [92].

### 5. DIFFUSION MECHANISMS IN THE Ti–Al SYSTEM

Theory of diffusion in alloys and compounds includes two basic aspects: (1) identification of the diffusion mechanism, i.e. the elementary atomic event or chain of events which governs the long-range atomic transport, and (2) calculation of the diffusion coefficient for the underlying diffusion mechanism. Diffusion in most metals and alloys occurs by the mechanism of nearest-neighbor (NN) jumps of single vacancies. Hence, in most studies the emphasis has been placed on accurate calculations of diffusion coefficients, which is a challenging problem especially in disordered alloys [52, 93]. In contrast, diffusion mechanisms in ordered intermetallic compounds are not well established at present, but it is well recognized that they are more complex, diverse, and generally different from those in metals and alloys [94–97]. This explains why most studies in this area are focused on the identification of diffusion mechanisms rather than accurate calculations of diffusion coefficients. In fact, even when diffusion coefficient are calculated, the purpose usually is to verify the adopted diffusion mechanism by comparing with diffusion coefficients calculated for other mechanisms or measured in experiments.

---

**Table 5. Effective formation energies of point defects in Ti$_3$Al and TiAl calculated from analytical expressions listed in Table 3**

<table>
<thead>
<tr>
<th>Ti$_3$Al</th>
<th></th>
<th></th>
<th>TiAl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al-rich alloy</td>
<td>Stoichiometric alloy</td>
<td>Ti-rich alloy</td>
</tr>
<tr>
<td>$V_{Ti}$</td>
<td>1.236</td>
<td>1.314</td>
<td>1.392</td>
</tr>
<tr>
<td>$V_{Al}$</td>
<td>2.039</td>
<td>1.805</td>
<td>1.570</td>
</tr>
<tr>
<td>$Al_{Ti}$</td>
<td>0</td>
<td>0.313</td>
<td>0.625</td>
</tr>
<tr>
<td>$Ti_{Al}$</td>
<td>0.625</td>
<td>0.313</td>
<td>0</td>
</tr>
<tr>
<td>Ti$_3$Al</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V_{Ti}$</td>
<td>0.932</td>
<td>1.153</td>
<td>1.374</td>
</tr>
<tr>
<td>$V_{Al}$</td>
<td>1.626</td>
<td>1.405</td>
<td>1.184</td>
</tr>
<tr>
<td>$Al_{Ti}$</td>
<td>0</td>
<td>0.442</td>
<td>0.884</td>
</tr>
<tr>
<td>$Ti_{Al}$</td>
<td>0.884</td>
<td>0.442</td>
<td>0</td>
</tr>
</tbody>
</table>
### Table 6. Analytical expressions and calculated energies (in eV) of composition-conserving point-defect complexes in TiAl obtained by first-principles methods [76] and with embedded-atom potentials (present work)

<table>
<thead>
<tr>
<th>Defect complex</th>
<th>$V_{Ti} + V_{Al}$</th>
<th>$A_{Ti} + Ti_{Al}$</th>
<th>$2V_{Ti} + Ti_{Al}$</th>
<th>$2V_{Al} + A_{Ti}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Expression</td>
<td>$E_v + e_v + 2e_0$</td>
<td>$e_{Al} + e_{Ti_{Al}}$</td>
<td>$2e_{v_{Ti}} + 2e_0 + e_{Ti_{Al}}$</td>
<td>$2e_{v_{Al}} + 2e_0 + e_{Al_{Ti}}$</td>
</tr>
<tr>
<td>Ref. [76]</td>
<td>3.582</td>
<td>1.204</td>
<td>3.775</td>
<td>4.593</td>
</tr>
<tr>
<td>Present work</td>
<td>2.557</td>
<td>0.884</td>
<td>2.744</td>
<td>3.251</td>
</tr>
</tbody>
</table>

In what follows we will be concerned with diffusion in the ordered compounds Ti$_3$Al and TiAl. Since very little is known about diffusion mechanisms in these specific compounds, we will first consider possible alternatives in the context of what is known about diffusion mechanisms in other, better studied compounds. Our analysis will be based for the most part on geometrical considerations rather than actual calculations, although some models and computational techniques applied for the evaluation of diffusion coefficients will be also reviewed on the way. Later, we will present our recent simulation results for diffusion in Ti$_3$Al and TiAl obtained with embedded-atom potentials.

### 5.1. General consideration

As in Section 4, it is convenient to discuss a generic binary compound A$_n$B$_m$, whose ground-state structure consists of two sublattices $x$ and $\beta$ filled, in a perfectly ordered state, with atoms A and B, respectively. We assume that diffusion in this compound is mediated by vacancy jumps between NNN sites. Direct vacancy jumps to next-nearest-neighbor (NNN) sites will not be considered here. While such jumps can be important in more open structures, such as the b.c.c.-based B2 structure of NiAl [68], they are most likely to be unimportant in the close-packed structures of Ti$_3$Al and TiAl.

A vacancy jump from one sublattice to the other creates an additional antisite defect. Because a random walk of a vacancy through an ordered structure would inevitably include inter-sublattice jumps, it would increase atomic disorder of the crystal. Therefore, in thermodynamic equilibrium vacancy jumps must be essentially correlated with one another and occur in a way that preserves the average degree of order. This requirement poses a strong selection rule on possible diffusion mechanisms. Perhaps the simplest way to preserve the order is to let vacancies travel along their own sublattices. We can also think of mechanisms consisting of chains of transitions such that the atomic order is first destroyed, but only locally and temporarily, and in the end of the chain is fully restored. Each individual transition is a single vacancy jump, but the chain may involve more than one vacancy and other point defects. The main requirement is that the initial and final states of the chain include the same set of defects and be symmetrically equivalent. Each chain results in net atomic displacements of two or more atoms, so that multiple repetitions of the chain can provide long-range atomic transport. The net displacements of atoms and defects resulting from an individual chain are often treated as “effective jumps”. If the chain starts (and ends) with a single vacancy with no other pre-existing defects involved, we talk about a cyclic mechanism. In a cyclic mechanism, the vacancy trajectory forms a loop, or a loop and a half, with some antisite defects first generated along the trajectory but later eliminated. Other mechanisms require two or more pre-existing defects, and are more likely to operate in off-stoichiometric compositions.

The principal possibility of a mechanism depends on the underlying ordered structure, but its actual importance relative to other mechanisms can only be evaluated by calculations. In the following we will consider several possible diffusion mechanisms in Ti$_3$Al and TiAl based on structural considerations. Their relative importance will be evaluated later.

### 5.2. Sublattice diffusion mechanism

The sublattice self-diffusion (SSD) mechanism can operate in structures where one or both sublattices form an infinite cluster, so that a vacancy can travel along a sublattice by NN jumps. In the DO$_19$ structure of Ti$_3$Al (Fig. 2), Ti sites form a penetrating sublattice, so that Ti self-diffusion can take place by vacancy jumps along that sublattice. In contrast, an Al atom is surrounded by Ti neighbors only, and NN jumps on the Al sublattice are not possible. In this respect the situation is similar to that in L1$_2$-type [97, 99, 100] and many other A$_3$B compounds. In all such compounds the minor element B is isolated, and its diffusion is more difficult than diffusion of the major element A. In most A$_3$B compounds the minor component is indeed a slower diffuser. This experimental observation, known as the Cu$_3$Au-rule [63], is also followed by Ti$_3$Al (see Section 3.2.1 and Table 2). The L1$_0$ structure of TiAl demonstrates a different situation: this structure consists of alternating (002) layers of Ti and Al atoms, so that both sublattices infinitely penetrate in the directions normal to the $c$-axis but none in the [001] direction parallel to the $c$-axis. Thus, diffusion in this compound must be not only anisotropic but also dominated by a different mechanism in either direction. While diffusion of both Ti and Al in directions normal to the $c$-axis can occur...
by the SSD mechanism, diffusion of both species along the c-axis involves inter-sublattice jumps, and thus requires some other mechanisms, which are yet to be established.

Because a penetrating sublattice, say \( z \), forms a three-dimensional (e.g. in \( Ti_3Al \)) or two-dimensional (e.g. in TiAl) periodic structure, sublattice self-diffusion of atoms A can be treated as the well known case of self-diffusion in a monoatomic crystal by the vacancy mechanism [93]. Note, however, that (i) the sublattice structure does not have to be isotropic, and (ii) the vacancy jumps do not have to be all equivalent to one another. If, however, all jumps are equivalent, the diffusion coefficient in a chosen direction \( x \) is given by

\[
D = f_0 g_x a^2 \Gamma. \tag{66}
\]

Here \( f_0 \) a correlation factor, \( g_x \) is a geometric factor which depends on the sublattice structure (e.g. \( g_x = 2/3 \) for any direction in \( L_12 \) structure [98]; \( g_x = 1 \) if \( x \) is normal to the c-axis and 0 if \( x \) is parallel to the c-axis in \( L_10 \) structure), \( a \) is the lattice period, \( x \) is the equilibrium vacancy concentration on the sublattice, \( \Gamma \) is the vacancy-atom exchange frequency.

Correlation factors for self-diffusion in different structures are either known or can be readily determined by Monte Carlo simulations. The vacancy concentration on the sublattice can also be calculated as discussed before (Section 4). The vacancy exchange frequency can be calculated from the harmonic transition state theory [100].

\[
\Gamma = v_0 \exp(-E_m/k_B T). \tag{67}
\]

\( E_m \) being the barrier of the jump (vacancy migration energy), \( v_0 \) the attempt frequency. For simulations in a periodic block, \( v_0 \) is given by the standard expression

\[
v_0 = \frac{3N-3}{3N-4} \frac{\prod_{i=1}^{N-1} \omega_i}{\prod_{i=1}^{N} \omega_i^*} \tag{68}
\]

where \( \omega_i \) and \( \omega_i^* \) are normal vibrational frequencies for the equilibrium vacancy configuration and the saddle point configuration, respectively.

Finding the saddle point is a special problem. While in many crystalline structures it can be identified from symmetry considerations, for sublattices with their generally lower symmetry this is often impossible. Perhaps the simplest regular procedure for finding the “reaction path” and the saddle point for a vacancy jump is offered by the “drag” method, which was extensively applied in the investigations of diffusion in NiAl [68, 80], as well as in grain boundary diffusion simulations [101]. In this method, the atom exchanging with the vacancy is advanced by small steps along the jump vector, i.e. vector connecting the initial and final equilibrium positions of the atom. After each step the energy of the block is minimized with respect to displacements of all other atoms. During the minimization, the jumping atom itself is also allowed to displace in directions normal to the jump vector, but not along the jump vector. In a periodic block, in order to prevent its rigid translation, an equal artificial counter-force is applied to every non-jumping atom so that to balance the force acting on the jumping atom. The trajectory made by the jumping atom in this process is not, generally, a straight line and represents the “reaction path”. The point at which the energy attains a maximum is identified as the saddle point, and the barrier \( E_m \) is determined as the saddle-point energy minus the initial energy. Although the “drag” method has shown excellent performance in most cases, it is known to fail in certain situations [102]. If necessary, a more powerful method must be applied, such as the recently developed “nudged elastic band” method [102].

Equation (66) does not apply if there are non-equivalent jumps on the sublattice. For example, non-basal jumps on the Ti sublattice in \( Ti_3Al \) are not equivalent to basal jumps. Moreover, even basal jumps on the Ti sublattice are not all equivalent to one another. The jump multiplicity makes the problem more complex. Equation (66) has to be properly generalized by averaging over all possible jump lengths (through factor \( g_x \)), exchange frequencies \( \Gamma \), and perhaps also the vacancy occupation probabilities \( X_v \) if these vary over the sublattice. The unique correlation factor \( f_0 \) must be replaced by partial correlation factors relating to different jumps. The partial correlation factors are not geometric constants but rather depend, in a complex manner, on all exchange frequencies, and thus on temperature. The vacancy migration through the sublattice is not a purely random walk anymore, but rather a correlated walk that can be described through a vacancy correlation factor \( f_c < 1 \) (“structural correlations” [103, 104]). While the latter can be readily calculated by either the determinant method of Ishioka and Koiwa [105] or the S-vector technique [104], the calculation of partial correlation factors of atoms is much more involved. Perhaps the easiest way to handle the problem is to calculate the diffusion coefficients directly by the kinetic Monte Carlo method. It is worth mentioning that this problem is similar to that of self-diffusion in grain boundaries, and one can take advantage of the methods and ideas developed in that area [101].

Vacancy jumps along a sublattice can also provide diffusion of the unlike element. Indeed, if sublattice \( z \) penetrates through the crystal and atoms \( B \) can go to that sublattice in the form of antisite defects \( B_x \), they can diffuse by exchanges with \( V_x \) vacancies. This “sublattice antisite diffusion” (SAD) mechanism has a close similarity to impurity diffu-
sion in dilute alloys, B\textsubscript{2}-antisites being the “impurity”. Accordingly, the classic models of impurity diffusion [93] can be adapted to the SAD mechanism with proper modifications if necessary. For example, the five jump-frequency model [106] was recently used to describe diffusion of element B along sublattice z in L\textsubscript{1}\textsubscript{\text{2}}-ordered A\textsubscript{2}B compounds [96, 98]. This model represents the diffusion coefficient of atoms B in the form

\[ D = f g_e a^2 X_V X_B (\Gamma_4 / \Gamma_3) \Gamma_2. \]  

(69)

Here \( \Gamma_2 \) is the vacancy-antisite exchange frequency, \( \Gamma_3 \) and \( \Gamma_4 \) are frequencies of dissociative and associative vacancy jumps, respectively, and \( f \) is the correlation factor. The latter can be expressed in terms of five frequencies: \( \Gamma \) (vacancy jump frequency on the sublattice far away from the antisite), \( \Gamma_1 \) (vacancy jump from a NN position of the antisite to another NN position), \( \Gamma_2, \Gamma_3 \) and \( \Gamma_4 \). The product \( X_V X_B \) represents the probability of the vacancy and antisite being nearest neighbors on the sublattice. The ratio \( \Gamma_4 / \Gamma_3 \) depends on the vacancy-antisite binding energy \( E_B \), i.e.

\[ \Gamma_4 / \Gamma_3 \propto \exp(-E_B / k_B T). \]  

(70)

Expressions for \( f \) are available for several structures (see, for example Ref. [96] and references therein), or can be derived for the sublattice in question. Again, if there is multiplicity of vacancy jumps on the sublattice, the above equations must be modified accordingly.

Antisite atoms B present on sublattice z may enhance or reduce the diffusivity of host atoms A on that sublattice. The effect is similar to the impurity-induced solvent diffusivity enhancement/retardation observed in some dilute bulk alloys, typically with a close-packed structure [93]. In such alloys, an enhancement is observed when a vacancy is attracted to an impurity atom and jumps around it, along its first coordination shell, faster than far away from the impurity. Such vacancy jumps intermix host atoms in the vicinity of the impurity faster than elsewhere, which results in overall enhancement of solvent self-diffusion. Using this analogy, the well-known expressions for the solvent-enhancement factor in bulk alloys (particularly those based on the five-jump frequency model) can be adopted, after proper modifications, for sublattice diffusion enhancement by antisites. This effect can play a role for Ti self-diffusion in Ti\textsubscript{2}Al, especially in Al-rich compositions. In TiAl, on the other hand, this effect cannot be very significant because the two-dimensional square-lattice structure of (002) layers does not support NN vacancy jumps along the first coordination shell of an atom, i.e. \( \Gamma_1 = 0 \). Thus, every jump of a vacancy neighboring an antisite is either a dissociative jump (\( \Gamma_3 \)) or an exchange with the antisite (\( \Gamma_2 \)).

### 5.3. Cyclic mechanisms

The simplest cyclic mechanism is a three-jump cycle (3JC) [7]. Under this mechanism, a vacancy makes a jump to the unlike sublattice, then another jump along that sublattice, and finally returns to its original position (Fig. 21). As a result, two atoms on the unlike sublattice (a and b in Fig. 21) exchange their positions. Thus, under this mechanism atomic jumps on one sublattice are induced by vacancies of the other sublattice. Depending on the nature of the vacancies, the defect reactions accompanying a 3JC cycle can be either

\[ V_z \rightarrow V_\beta + B_z \rightarrow B_\beta + V_\beta \rightarrow V_z \]  

(71)

\[ V_\beta \rightarrow V_z + A_\beta \rightarrow A_\beta + V_\beta \rightarrow V_\beta. \]  

(72)

The respective cycles are called \( z \)-3JC and \( \beta \)-3JC. The antisite created during a 3JC is eliminated in the end. For this mechanism to work, the sublattice on which the atoms move must penetrate through the crystal, while the sublattice on which the vacancies reside does not have to possess this property.

The diffusion coefficient can be written down in the form of equation (66), but with the vacancy concentration on the unlike sublattice. Thus, the diffusion coefficient of atoms A will depend on \( X_V \),

\[ D_A = f g_e a^2 z X_V \Gamma, \]  

(73)

and vice versa. Here \( z \) is the number of 3JCs which can induce the given jump of atom A, \( \Gamma \) is the effective frequency of each cycle. In terms of the mean first passage time (MFPT) theory [107, 108],

\[ \Gamma = P / \bar{t}, \]  

(74)

where \( \bar{t} \) is the mean expectation time of any 3JC performed by a vacancy \( V_\beta \). \( P \) is the probability of the specific cycle which will induce the given atomic jump. Both quantities \( \bar{t} \) and \( P \) can be calculated along the lines of Ref. [109] where the MFPT theory was applied for the analysis of six-jump vacancy cycles in B\textsubscript{2} structure. Using the MFPT formalism, \( \bar{t} \) and \( P \) can be expressed in terms of individual vacancy jump frequencies, which in turn can be calculated from equations (67) and (68). MFPT calculations take into account that some of the vacancy jumps along the cycle can be reversed, so that the actual number of jumps made by a vacancy is more than three. They also take into account the multiplicity of 3JCs that can be implemented after the first vacancy jump.

The calculation of the correlation factor \( f \) is the most difficult task. Because the vacancy always returns to its original position, there is a larger than random probability that the atomic displacements induced by the previous cycle will
be reversed by the next one. We can consider two extreme cases here. Suppose vacancies $V_β$ are highly mobile on their own sublattice $β$. Then, upon completion of a 3JC the vacancy will have a high probability to jump away from the pair of swapped A-atoms along the $β$-sublattice. The next move of either of these A-atoms will be, then, induced by either a “fresh” vacancy or the same one but approaching the atoms from a random direction. The movements of atoms A will be virtually uncorrelated, and $f$ will be close to unity. In the other extreme, the vacancies can be highly immobile (e.g. when atoms B are isolated from one another). In that case, a single vacancy $V_β$ will only move atoms A back and forth along its first coordination shell without any advancement to larger distances. The atomic-jump correlations will be extremely high and $f$ extremely small ($f → 0$). In a general case, the 3JC mechanism will be coupled, through the correlation factor, with the mechanism responsible for long-range transport of vacancies implementing the cycles. This aspect of the 3JC mechanism has never been analysed in greater detail.

In the structure of TiAl, 3JC of Al vacancies can provide diffusion of Ti atoms along their sublattice, and vice versa (Fig. 22). An Al vacancy can initiate 4 3JC to each of the two adjacent Ti layers, each 3JC having a probability of $P = 1/3$. Every displacement of a Ti atom can be induced by 4 3JC, so that $z = 4$. As mentioned before, the diffusivity of Ti atoms by this mechanism will depend, through the correlation factor, upon the sublattice diffusivity of Al vacancies, and vice versa.

In Ti$_3$Al, Ti diffusion can be induced by 3JC of Al vacancies. There are three types of 3JC in this

![Fig. 21. Schematic illustration of diffusion mechanisms in an ordered compound: three-jump cycle (3JC), six-jump cycle (6JC), and anti-structural bridge (ASB). The numbers indicate the sequence of vacancy jumps.](image1)

![Fig. 22. Schematic three-jump cycles of Al vacancies in Ti$_3$Al (a) and TiAl (b). The numbers indicate the sequence of vacancy jumps. In Ti$_3$Al, two basal-plane and one non-basal-plane cycles are indicated.](image2)
structure (Fig. 22): (1) basal cycles, which can provide Ti diffusion along basal planes, (2) non-basal cycles that also provide Ti diffusion along basal planes (the vacancy and the Ti atoms are in different basal planes), and (3) non-basal cycles that provide Ti diffusion between basal planes. A rigorous calculation of the diffusion coefficient is a difficult task. Not only does this require a model for Al diffusion, but also equations (73) and (74) need to be modified to include the non-equivalence of different cycles in this structure.

The 3JC mechanism requires the existence of triangles of NN bonds, and is therefore limited to close-packed structures. In contrast, the six-jump cycle (6JC) mechanism is more general, in that it can operate in more open structures as well. This mechanism was proposed by Huntington and studied in more detail by Elcock and McCombie [110]. As illustrated in Fig. 21, the 6JC mechanism consists of six NN jumps of a vacancy between four atomic sites, two of which belong to one sublattice and two to the other. The cycle results in two type of displacements: (1) the vacancy exchanges positions with an atom of the same sublattice (say, z), and (2) two atoms (a and b in Fig. 21) of the unlike sublattice (β) swap their positions. Note that these two atoms may or may not be nearest neighbors. If they are nearest neighbors, there is always a chance that the vacancy will make a direct jump a → b and the 6JC will turn into a 3JC. Like 3JCs, 6JCs do not need any pre-existing defects other than a vacancy. In contrast to 3JCs, however, the 6JC mechanism is not coupled with any other mechanism.

Since there are more jumps involved, 6JCs create more local disorder than 3JCs, but in the end the order is completely restored. Depending on the nature of the initial vacancy (Vz or Vβ), there can be two types of 6JC, which can be denoted as x-6JC and β-6JC, respectively [111]. The defect reactions accompanying an x-6JC are

\[ V_z \xrightarrow{1} V_\beta + B_z \xrightarrow{2} V_z + B_z + A_\beta \xrightarrow{3} V_\beta + B_z + B_z + A_\beta \xrightarrow{4} V_z \]

and similarly for a β-6JC. Here, the numbers above the arrows number the vacancy jumps. These reactions show a symmetry with respect to the “central” configuration \( V_\beta + 2B_z + A_\beta \) arising after the third jump. This does not necessarily mean that the energy along the cycle must also show this symmetry, because pairs of states which include the same set of defects may have different spatial configurations. In some cubic structures, e.g. in B2, all such pairs of configurations are indeed symmetrically equivalent, and the energy-displacement curves show mirror symmetry against the “central” configuration [68, 109]. In other structures however, like the DO19 structure of Ti3Al, the symmetry of some 6JCs is broken. Because atoms A and B are moved by 6JCs simultaneously, the diffusion coefficients of both species are strongly correlated. For example, for B2 compounds it was shown [109, 112] that the ratio of the diffusion coefficients lies between \( q \) and \( 1/q \), where \( q \) is about 2.

The 6JC mechanism has been studied most extensively for the L12 and especially B2 structures. Belova et al. [113] applied Monte Carlo simulations within a two-frequency model to evaluate the efficiency of 6JCs in B2 structure. They concluded that this mechanism is only efficient in highly ordered states, and becomes less important as the long-range order decreases with increasing temperature and/or off-stoichiometry. This conclusion was recently confirmed [95, 114] by simulations within a more general, four-frequency model. While in highly ordered states the ratio \( D_A / D_B \) was indeed confined within the limits mentioned above, in more disordered states this ratio varied widely, thus indicating the involvement, or even predominance, of other mechanisms. Athénès et al. [111] performed a very detailed Monte Carlo study of different cycles in a B2 compound. They used a broken-bond kinetic model in conjunction with highly efficient residence time algorithms, allowing them to screen out multiple reverses of highly correlated vacancy jumps. It was again confirmed that the efficiency of 6JCs is limited to low temperatures and strongly ordered states. At higher temperatures 6JCs are influenced by existing antisites, which results in new effects such as antisite-assisted 6JCs, formation of dynamic vacancy-antisite complexes, looping of 6JCs, etc. These effects reduce the efficiency of the 6JC mechanism per se. To our knowledge, no Monte Carlo simulations have ever been performed for diffusion in either DO19 or L10 structures.

Usually there are several variants of a 6JC, which differ in effective jumps of atoms [109]. Some variants are symmetrically equivalent to one another, others are not. The effective diffusion coefficient of atoms A in direction x due to x-6JCs can be written as

\[ D_A = \frac{1}{2} \sum_i f_i \lambda_i^2 \Gamma_i \]  

Here the geometric factors \( \gamma_i \), the partial correlation factors \( f_i \), the projected jump lengths \( \lambda_i \) and the transition frequencies \( \Gamma_i \) relate to all possible effective jumps i. A similar expression holds for the diffusion coefficient of atoms B. The partial correlation factors can be evaluated by combining the matrix method [52] with a simple model for next-jump probabilities [109]. More accurate calculations of the diffusion coefficients can be performed
by the Monte Carlo method using $\Gamma_s$ as input data.

The transition frequencies $\Gamma_i$ can be determined from the MFPT-theory expression

$$\Gamma_i = P_i / \bar{t},$$

which was first applied to 6JCs in B2 compounds [109]. Here $\bar{t}$ is the mean expectation time to complete a 6JC, $P_i$ is the probability that the cycle will result in a given atomic jump $i$. Analytical expressions for $\bar{t}$ and $P_i$ were originally derived for the B2 structure [109], but can be worked out for the DO19 and L10 structures as well. We would like to mention that alternatively, and perhaps more easily, $\bar{t}$ and $P_i$ can be determined by Monte Carlo simulations. Indeed, the MFPT-theory derivations for these quantities actually consider a random walk of a particle on a configurational cluster formed by all possible states arising during a 6JC process. The connectivity of the cluster represents all possible transitions, as well as their reversals and switches between geometrical variants of a cycle (see e.g. Fig. 3 in Ref. [109] or Fig. 3 in Ref. [68]). Multiple random walks on this cluster can be simulated directly by a residence-time Monte Carlo technique, in which a walk stops as soon as the particle reaches a terminal state (cycle completion). From such simulations, $\bar{t}$ and $P_i$ can be deduced by averaging over the durations of the walks and different types of termination, respectively. The improved residence–time techniques [111] could be conveniently used for the elimination of multiple reversals.

In Ti$_3$Al, there are two types of 6JC (Fig. 23). An Al–6JC induces an Al-atom jump between basal planes (0002) and simultaneously swaps two Ti atoms in the initial basal plane of the vacancy. Because the two Ti atoms are first neighbors, the cycle can be interrupted and switched to a 3JC process. A Ti–6JC induces a NN jump of a Ti atom in a basal plane and swaps two Al atoms lying in adjacent (0002) planes. These Al atoms are not first neighbors, so there is no risk of switching to a 3JC process. Note that in both cases Al atoms make effective jumps between adjacent basal planes, while Ti atoms move in basal planes only. Thus, the 6JC mechanism gives no contribution to Ti diffusion parallel to the c axis.

TiAl supports a greater diversity of 6JCs. For example, a Ti vacancy can make one of three effective jumps: $\frac{1}{2}[110]$, $[001]$ and $\frac{3}{2}[112]$, in each case by exchanging two Al atoms in a (002) plane. In all these cycles, which are not shown in Fig. 23, the Al atoms are nearest neighbors, so that the 6JCs can be interrupted by 3JCs. There is one type of a 6JC that might be most important for diffusion. In this cycle (Fig. 23), a Ti vacancy makes a [100] jump and exchanges two Al atoms in different (001) layers, so that each Al atom makes a NNN jump by a vector $\pm[001]$. This cycle cannot switch to a 3JC. Similar considerations hold for Al–6JCs. Thus, the 6JC mechanism has a potential to contribute to Ti and Al diffusion both normal and parallel to the c axis.

It should be mentioned that, besides 3JCs and 6JCs, there can be longer vacancy cycles [115], but their efficiency decreases as the number of jumps increases. Such cycles will not be considered here.

5.4. Anti-structural bridges

At elevated temperatures and/or in off-stoichiometric compositions the concentration of anti-structural defects increases. At some point they can form a percolating substructure on which atoms can freely diffuse through the crystal without affecting its average degree of order. This substructure, or a percolating cluster, can be viewed as made of “bridges”, i.e. atomic configurations allowing a vacancy to make long jumps without increasing the number of antisites. This “anti-structural bridge” (ASB) mechanism was first proposed for B2 compounds [116] and later extended to other structures [7, 34, 95, 99, 117]. In contrast to cyclic mechanisms, the ASB mechanism requires not only vacancies but also pre-existing antisites. An elementary bridge event involves one vacancy and one antisite, and consists of two NN jumps of the vacancy. These jumps result in NN displacements of two atoms of the same species.

Fig. 23. Schematic six-jump cycles in Ti$_3$Al (a) and TiAl (b). The numbers indicate the sequence of vacancy jumps. In TiAl, only one type of cycle is shown for simplicity.
We would like to point out that there can be two different types of ASB. In one type, which we will call ASB1, the vacancy and the antisite belong to the same sublattice, say $a$. The vacancy first exchanges with a regular atom on sublattice $b$ and then with the antisite,

$$V_a + B_a \rightarrow V_b + B_a + V_b.$$  \(78\)

These exchanges induce displacements of two atoms B. The extra antisite $B_a$ created by the first jump is eliminated by the second jump, so that the initial order gets restored. This process can only continue if there is another $B_a$-antisite around the vacancy in its new position. Note that atoms B are moved by vacancies of sublattice $a$, and vice versa. Therefore, the diffusion coefficient is proportional to the product of vacancy and antisite concentrations on the unlike sublattice,

$$D_A \propto X_{V_a} X_{A_{a}}.$$  \(79\)

$$D_B \propto X_{V_b} X_{B_b}.$$  \(80\)

This type of bridges was first introduced in Ref. [116] in relation to B2 compounds, but they can be found in other structures as well.

In the second type of bridges (ASB2), introduced in Ref. [7], the vacancy and the antisite belong to different sublattices and are initially nearest neighbors. The vacancy (say, $V_b$) first exchanges with the antisite ($B_a$) and then with a regular atom on sublattice $b$,

$$V_b + B_a \rightarrow V_a + B_a + V_b.$$  \(81\)

Again, these exchanges induce displacements of two atoms B. The process will continue if there is another $B_a$-antisite near the vacancy in its new position. Under this mechanism, vacancies induce jumps of like atoms assisted by anti-structural defects on the unlike sublattice. Accordingly, for the diffusion coefficients we have

$$D_A \propto X_{V_b} X_{A_b},$$  \(82\)

$$D_B \propto X_{V_b} X_{B_b}.$$  \(83\)

There is a close relation between vacancy jumps under the ASB2 and 3JC mechanisms [7].

Generally, both ASB1 and ASB2 processes can be implemented by either kind of a vacancy. There can be, thus, four different types of bridge: $a$-ASB1 and $a$-ASB2 (with a vacancy on sublattice $a$), as well as $b$-ASB1 and $b$-ASB2 (with a vacancy on sublattice $b$). Atoms A are moved by bridges $b$-ASB1 and $a$-ASB2, while atoms B are moved by bridges $a$-ASB1 and $b$-ASB2.

Due to the percolative nature of the ASB mechanism, the diffusion coefficients do not lend themselves to rigorous analytical calculations. Even the threshold antisite concentrations, at which the bridges first form a percolating cluster, can only be determined by Monte Carlo simulations [95, 117, 118]. The threshold concentrations are essential for the evaluation of the temperature/concentration domain in which the ASB mechanism can dominate the diffusion process. It should be pointed out, however, that the ASB mechanism can be operative also below the percolation threshold, except that the atomic displacements will be confined to finite clusters formed by ASBs. If diffusion within such clusters is faster than diffusion between them, ASBs can still enhance the overall diffusion rates in the crystal. But of course, the enhancement effect will not be as strong as it becomes above the percolation threshold. As an additional complication, the ASB mechanism can be coupled with other mechanisms, especially if there is a continuous sublattice in the structure. In the latter case, an ASB process can always be interrupted, or even aborted, by vacancy jumps away from the antisite(s). Some other interesting effects associated with the ASB mechanism in such structures are discussed in Ref. [95].

The DO19 structure of Ti$_3$Al supports all four types of ASB introduced above. Each type of a bridge has several geometrically different variants and can induce both basal and non-basal jumps. This applies equally to the L1$_0$ structure of TiAl. For simplicity, in Fig. 24 we only illustrate a Ti-ASB1 and Al-ASB2, both of which induce...
non-basal jumps of Al atoms. See also Fig. 11(b) in Ref. [7] for a Ti-ASB2.

There are other diffusion mechanisms, such as the triple-defect and di-vacancy mechanisms [119], which were not considered here. While of potential importance in B2 compounds, they do not seem to be important for diffusion in Ti3Al or TiAl.

\subsection{5.5. Calculation results for Ti3Al and TiAl}

Calculations for Ti3Al and TiAl were performed by molecular statics with embedded-atom potentials. Some of our results for TiAl were reported in Ref. [7], while all other results were obtained in this paper. Most technical details of our calculations were already described in Section 4.2. The barriers of vacancy jumps, $E_m$, were determined by the “drag” method (Section 5.2). Each jump was implemented in both directions in order to verify its reversibility. Figure 25 shows energy–displacement curves for the 6JC mechanism in Ti3Al (these cycles are illustrated in Fig. 23). Although it may not be seen immediately, the curve for the Al–6JC, in contrast to that for the Ti–6JC, is not perfectly symmetrical for the reasons discussed in Section 5.3.

The approach taken in our calculations was as follows. For each diffusion mechanism, its activation energy $Q$ was evaluated based on simplifying assumptions. The relative importance of different mechanisms was evaluated by comparing the obtained activation energies, assuming that mechanisms with smaller $Q$ values make greater contributions to the overall diffusion process than mechanisms with larger $Q$ values. The activation energy $Q$ was estimated as

$$Q = \sum_{P} E_f^P + E_m,$$

where $E_f^P$ are effective formation energies of the point defects which initiate the mechanism, $E_m$ is an effective migration barrier for the mechanism. For multi-jump mechanisms, $E_m$ was estimated as the difference between the largest saddle-point energy over all jumps and the energy of the initial configuration. Equation (84) simply assumes that the diffusion coefficient is proportional to the probability of the initial configuration, which in turn is proportional to the product of the respective point defect concentrations, times the probability of implementing the elementary diffusion event which governs the chosen mechanism (a vacancy jump or a chain of jumps). The latter probability is assumed to be proportional to $\exp(-E_m/k_B T)$. Equation (84) neglects all binding energies between point defects. It also neglects all jump-correlation effects, which in many cases are temperature-dependent and thus contribute to $Q$.

This approach tacitly assumes that different mechanisms have about the same pre-exponential factor of diffusion, $D_0$, although in reality the entropy factors, different geometric coefficients and other effects may lead to significant variations in $D_0$. Overall, it should be recognized that this approach is highly approximate and should not be viewed as a replacement of accurate calculations of diffusion coefficients. However, equation (84) can be very useful for a quick evaluation of different diffusion mechanisms. Although the results can be inconclusive if two mechanisms have comparable activation energies, at least we can rule out highly unfavorable mechanisms and select those which deserve a further analysis by more rigorous methods.

In Table 7 we summarize analytical expressions

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Ti diffusion</th>
<th>Al diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti3Al: SSD</td>
<td>$E_{V_{Ti}} + E_{V_{Al}}$</td>
<td>0.833</td>
</tr>
<tr>
<td>SSD</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>0.680</td>
</tr>
<tr>
<td>Al–3JC</td>
<td>$E_{V_{Ti}} + E_{V_{Al}}$</td>
<td>0.680</td>
</tr>
<tr>
<td>6JC</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.875</td>
</tr>
<tr>
<td>6JC</td>
<td>$E_{V_{Ti}} + E_{V_{Al}}$</td>
<td>1.875</td>
</tr>
<tr>
<td>Ti–ASB1</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.210</td>
</tr>
<tr>
<td>Al–ASB2</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>0.761</td>
</tr>
<tr>
<td>TiAl: SSD</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.456</td>
</tr>
<tr>
<td>SSD</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.414</td>
</tr>
<tr>
<td>Al–3JC</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
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<tr>
<td>Ti–3JC</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.822</td>
</tr>
<tr>
<td>Ti–6JC</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.967</td>
</tr>
<tr>
<td>Al–6JC</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>2.410</td>
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<tr>
<td>Al–ASB1</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.782</td>
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<tr>
<td>Ti–ASB2</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>0.712</td>
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<td>Ti–ASB1</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
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</tr>
<tr>
<td>Al–ASB2</td>
<td>$E_{V_{Ti}} + E_{V_{Al}} + E_{m}$</td>
<td>1.323</td>
</tr>
</tbody>
</table>

* Different $\pm$ only.

In Table 7 we summarize analytical expressions for the activation energy $Q$ and numerical values of the effective migration energy $E_m$ (in eV) under different diffusion mechanisms in Ti3Al and TiAl. Mechanisms: SSD, sublattice self-diffusion; SAD, sublattice anti-site diffusion; 3JC, three-jump cycles; 6JC, six-jump cycles; ASB1 and ASB2, anti-structural bridges of types 1 and 2.
for $Q$ under several mechanisms, together with the obtained $E_m$ values. This table includes only mechanisms selected above from structural considerations. For Ti diffusion in Ti$_3$Al, we have a priori excluded the ASB mechanism because, given the low activation energy of Ti diffusion on its own sublattice (SSD mechanism), the existence of ASBs does not seem to be very important. In cases when there were several geometric variants of the mechanism, we included the lowest $E_m$ value. 6JC's in TiAl were represented by [001]-type cycles illustrated in Fig. 23(b).

Because the defect formation energies $E_f^P$ are functions of composition (Section 4), the activation energy $Q$ is also a function of composition. In Fig. 26 we show functions $Q(c_{Ti})$ obtained by combining our $E_m$ values with functions $E_f^P(c_{Ti})$ calculated in Section 4. The curves for the ASB mechanism are shown by dashed lines as a reminder that this mechanism only works in essentially off-stoichiometric compositions or at very high temperatures.

For Ti diffusion in Ti$_3$Al [Fig. 26(a)], the SSD mechanism obviously provides the easiest diffusion path. 3JC's of Al vacancies are generally more difficult, but become increasingly more efficient with increasing Ti concentration. In Ti-rich compositions the Al-3JC mechanism may compete with the SSD mechanism. 6JC's do not seem to be important at any composition. Al diffusion [Fig. 26(b)] is obviously dominated by antisite-vacancy exchanges on the Ti-sublattice (SAD mechanism), as was predicted earlier from the analysis of experimental data for Ga diffusion [34]. 6JC's of Al vacancies can compete with the SAD mechanism in Ti-rich compositions. ASBs do not appear to be very important, except perhaps in Al-rich compositions. However, the composition and temperature ranges in which the ASB mechanism can be operative in the DO$_{19}$ structure cannot be specified since the respective percolation threshold is not known.

Ti diffusion in TiAl [Fig. 26(c)] is dominated by vacancy diffusion along Ti layers (SSD). In Ti-rich compositions this mechanism becomes less effective, but at the same time Ti diffusion along Al layers...
(SAD mechanism) becomes more favorable. Note that both mechanisms provide diffusion normal to the $c$ axis only, as does also the Al-3JC mechanism. The only mechanism that supports diffusion across [001] layers is the 6JC mechanism, which has a relatively large activation energy. This observation suggests that the diffusion anisotropy of Ti in TiAl can be very strong at low temperatures. At high temperatures and/or significant deviations from stoichiometry, the ASB mechanism may come into play. This would reduce the diffusion anisotropy. The Ti–ASB2 mechanism is very favorable, but the bridges never form a continuous substructure. At stoichiometry, the percolation threshold for this mechanism is never reached even at high temperatures, although fast diffusion along ASBs within finite clusters can still reduce the anisotropy and enhance the diffusivity. This contribution of ASBs at high temperatures was suggested [7] as an explanation of the non-Arrhenius behavior of Ti self-diffusion in TiAl (see Fig. 16). Deviations from stoichiometry would not allow the alloy to reach the percolation threshold either, but ASBs can still enhance the diffusivity, especially in Ti-rich compositions. Al diffusion [Fig. 26(d)] also occurs predominantly along Al layers (SSD mechanism), but in Al-rich compositions Al can also diffuse along Ti layers (SAD). Again, 6JC is the only mechanism capable of providing diffusion parallel to the $c$ axis at low temperatures. ASBs can enhance diffusion in Al-rich compositions, but are less efficient at stoichiometry and highly unfavorable in Ti-rich compositions. It follows that Al diffusion in TiAl must be more anisotropic and, on average, more difficult than Ti diffusion.

Thus, our calculations suggest that Al is a slower diffuser than Ti in both compounds. This trend is generally consistent with experimental data (Table 2). However, the calculated activation energies of Al diffusion are not as high as the experimental values deduced from the Darken–Manning equation (Section 3.2). On the other hand, the calculated differences between the activation energies of Ti and Al are comparable with the experimental differences observed for diffusion of Ga [34] as a representative of Al.

Overall, the calculated activation energies are consistently lower than the experimental values. This trend may have several sources. Firstly, in our calculations we always used the lower estimates of the migrations barriers. Secondly, by neglecting all correlation effects we could have overestimated the efficiency of some mechanisms, especially those which involve multiple jumps (such as 6JC). Last but not least, the embedded-atom potentials employed in this work were not designed for accurate diffusion calculations, and in particular could systematically underestimate all vacancy migration barriers. This kind of underestimation is a common feature of most embedded-atom potentials. For example, for self-diffusion in $\alpha$-Ti the present potential predicts $Q = 2.2$ eV, which is lower than the experimental value 3.14 eV [10]. Experience shows that, despite the underestimated barriers, good-quality embedded-atom potentials usually do represent the right trends in diffusion behavior. Nevertheless, the significant discrepancies between calculated and measured activation energies observed in this work call for using more accurate atomic interaction models in future diffusion studies of the Ti–Al system.

6. CONCLUSIONS

Due to our recent efforts, experimental data are now available for Ti and Al diffusion in $\alpha$-Ti(Al), $\beta$-Ti(Al), and intermetallic phases $\gamma_2$-Ti$_3$Al and $\gamma$-TiAl. These data show “normal” diffusion behavior and follow established empirical rules, including the Cu$_3$Au-rule, the retardation effect of ordering on diffusion, etc. Diffusion of Ti in these phases was measured with the radioactive isotope $^{44}$Ti. Al diffusion in pure $\alpha$-Ti and $\beta$-Ti was measured by the SIMS technique. Due to the unavailability of a suitable radio-isotope of Al, direct radiotracer measurements of Al diffusion were not possible. Hence, Al diffusion in Al-containing phases was evaluated indirectly in two ways. Firstly, Al diffusion coefficients were calculated from the Darken–Manning equation using our Ti self-diffusion data and the data for interdiffusion. Secondly, gallium was chosen as a substitute element for Al, and its radiotracer diffusion was measured in all four phases of the system. The absolute values of the diffusion coefficients obtained both ways are close to one another, especially in the intermetallic compounds. However, the activation energies calculated through the Darken–Manning equation are consistently higher than those obtained for Ga diffusion. Analysis shows [34] that using Ga as a substitute for Al gives more reliable information on Al diffusion. Calculations from the Darken–Manning equation are associated with large errors in the activation energy, not to mention the issue of applicability of that equation to the ordered phases Ti$_3$Al and TiAl. Both methods indicate, however, that Al diffuses in Ti$_3$Al and TiAl slower, and with a higher activation energy, than Ti. The obtained diffusion coefficients of Ti and Al and their temperature and concentration dependencies provide valuable information for the evaluation of diffusion-controlled processes in Ti–Al alloys.

Impurity diffusion in the Ti–Al system has also been investigated in a systematic way. All impurities studied so far can be classified into normal and fast diffusers. For some normal diffusers, our data allow us to predict their diffusion mechanism, as well as their sublattice occupation preferences in the compounds. The fast-impurity effect, observed for some transition elements (e.g. Fe, Co and Ni), is strongest
in \(\gamma\)-Ti, weaker in \(\beta\)-Ti and \(\text{Ti}_3\text{Al}\), and small in \(\text{TiAl}\). The effect can be explained by a partially interstitial solubility of fast impurities in the lattice and their diffusion by an interstitial-related mechanism. Apparently, the trend to interstitial solubility sensitively depends on the availability of Ti atoms in the local environment of an interstitial atom.

As a next step, the diffusion studies could be extended to grain boundaries in individual phases, as well as interphase boundaries between them. The \(\gamma/\gamma\) and \(\gamma_2/\gamma\) interfaces would be of special interest in view of their importance in determining the mechanical behavior of intermetallic alloys. Although preliminary data are available for grain boundary diffusion, there is much work to be done in this area.

On the theoretical side, issues of prime importance are the calculation of point-defect concentrations as functions of temperature and composition, and identification of atomic mechanisms of diffusion in the intermetallic compounds. The point defect concentrations can be determined from the statistical–mechanical model described in this paper (Section 4), given the so-called “raw” free energies of individual point defects. These latter, in turn, can be determined by molecular statics in conjunction with the harmonic approximation. Such calculations require a model describing atomic interactions in the \(\text{Ti}–\text{Al}\) system. In this paper, calculations were performed using embedded-atom potentials. The obtained point defect concentrations and effective formation energies confirm the antisite-disorder mechanism in both \(\text{Ti}_3\text{Al}\) and \(\text{TiAl}\), and provide input data for our diffusion calculations. However, the observed discrepancies with defect formation energies obtained in previous first-principles calculations suggest that point defect energetics in these compounds should be revisited with more accurate atomic interaction models.

We have analyzed possible diffusion mechanisms in \(\text{Ti}_3\text{Al}\) and \(\text{TiAl}\) by using the methodology and specific mechanisms proposed for other, better studied compounds, and considering specific features of the \(\text{DO}_{19}\) and \(\text{L}_1_0\) structures (Section 5). This analysis also revealed some new general aspects, such as the existence of two types of anti-structural bridges in compounds, possible asymmetry of six-jump cycles, and possible coupling of JCs and ASBs with other mechanisms. Together with the identification of the methods which can be applied for rigorous calculations of diffusion coefficients under different mechanisms, this analysis sets up a framework for future theoretical research on diffusion in titanium aluminides. As a first step on this way, we have carried out preliminary calculations based on embedded-atom potentials and a simplified estimation of diffusion activation energies. The results are in general agreement with experimental data. The obtained activation energies as functions of composition (Fig. 26) have allowed us to select a few most favorable mechanisms for future analysis by more accurate methods. Again, more adequate atomic interaction models are essential for future progress. In view of significant directional bonding in titanium aluminides [92], modified embedded-atom [120] or bond-order [121, 122] potentials could generate more reliable input data for our diffusion calculations. At further stages, diffusion simulations in grain and interphase boundaries of the Ti–Al system would be of great interest and practical importance.

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