OVERVIEW

Diffusion in Intermetallics

Helmut Mehrer

Institut für Metallforschung, Universität Münster, Wilhelm-Klemm-Strasse 10, D-48149 Münster, Germany

Intermetallic compounds or ordered alloys (intermetallics) have recently attracted much attention as materials for high-temperature applications. Diffusion is fundamental and ubiquitous in the art and science dealing with solid materials at elevated temperatures. A knowledge of the diffusion behaviour of intermetallics is therefore of interest for the production of these materials and for their use in technological applications. Whereas diffusion in many pure metals and dilute alloys is thoroughly investigated and reasonably well understood, systematic diffusion studies for intermetallic compounds are relatively scarce. An atomistic understanding of diffusion in intermetallics in terms of defect structure and diffusion mechanisms is obviously more complex than for metallic elements.

This overview is devoted to binary intermetallics. The reader is reminded of the more frequent structures (B2-, L1₂-, D0₃-, D0₁₉-, L1₀- and cubic Laves-type structures) of intermetallics. Some structural implications for diffusion in these materials including the Cu₃Au rule are considered. Various diffusion phenomena in binary systems like self-diffusion, diffusion of foreign atoms, single-phase and multiphase interdiffusion are described and illustrated by experimental examples from our laboratory. Some limitations of the Darken-Manning equation, which is sometimes used to correlate tracer diffusion of components and interdiffusion, are discussed.

Self-diffusion of components—the most basic diffusion process in solids—is reviewed for intermetallics with the above mentioned structures. Relevant factors for self-diffusion like the crystal structure, the state of order and disorder, the temperature and composition dependence are illustrated. In a few cases diffusion of selected foreign elements will also be considered. Particular attention will be devoted to our present understanding of diffusion in terms of defect structure and atomic mechanisms. This review also includes a summary of recent investigations on diffusion in the D0₃-type intermetallic compound Fe₃Si, Ti self-diffusion in intermetallic compounds of the Ti-Al system and single-phase and multiphase interdiffusion in various intermetallics including the cubic Laves-phase Co₂Nb.

(Received December 25, 1995)

Keywords: *intermetallics, self-diffusion, interdiffusion, multiphase diffusion, reaction diffusion, parabolic growth, Darken's equation, thermal vacancies, antisite defects, triple defects, diffusion mechanism*

I. Introduction

Binary intermetallics—on which we will concentrate in this overview—comprise compounds of two metals (or of a metal and a semimetal) whose crystal structures are different from those of the elements. This definition includes both, intermetallic phases and ordered alloys. Intermetallics are a fascinating group of materials which attract increasing attention in materials science from the viewpoints of fundamentals as well as the applications⁽¹⁾. In the past intermetallics with outstanding physical properties had already triggered the development of functional materials like, for example, superconductors based on A15 compounds (Nb₃Sn), shape-memory alloys (NiTi), high permeability materials (Ni₃Fe), permanent magnets (Co₅Sm) and others (see, *e.g.*, Table 1 in Ref. (1) for further examples). In contrast to their established use as functional materials intermetallics did not find many applications as structural materials until recently. The main hindrance was their brittleness at room temperature. In the meantime many efforts have been devoted to applications of intermetallic phases and ordered struc-

tures as structural materials. This is due to promising mechanical and corrosion properties at high temperatures of several intermetallics like for example the aluminides. An outstanding overview on the origins, status and future of structural intermetallics has been published by Westbrook⁽²⁾. Several reviews about mechanical properties of intermetallic compounds⁽³⁾⁽⁴⁾ and the recent books on intermetallics by Westbrook and Fleischer⁽⁵⁾ and by Sauthoff⁽¹⁾ should be consulted for further information about structure, defects and properties of intermetallic compounds. A very recent state-of-the-art overview of defect structures in intermetallic compounds was given by Yamaguchi and Shirai⁽⁶⁾.

Diffusion is a process which is very fundamental and ubiquitous in the art and science dealing with solid matter at elevated temperatures. A knowledge of the diffusion behaviour of intermetallics is therefore important for the production of these materials and for their practical use. For example, the high-temperature strength of intermetallics is limited by creep processes which are controlled by diffusion (see, *e.g.*, Ref. (7)). Despite of several reviews^{(8)–(13)} and of recent international conferences on diffusion⁽¹⁴⁾⁽¹⁵⁾ the information on diffusion in inter-

metallics is still scarce. As can be seen from a critical collection of diffusion data for metals and alloys edited by the present author⁽¹⁶⁾, the number of comprehensive diffusion studies on intermetallics is certainly by at least one order of magnitude smaller than the number of studies carried out for pure metals and dilute alloys.

Of course, there are reasons for this unsatisfactory situation. Studies of diffusion in intermetallics are in general considerably more laborious than for metallic elements: Homogenous, homo-phase starting materials may be difficult to prepare. The investigation of diffusion of both components in a single binary intermetallic as function of temperature and composition requires a considerable number of tedious measurements. Diffusion coefficients often depend strongly on the composition. Therefore, a careful characterization of the sample composition is necessary. In some of the earlier publications the characterization of the sample material was insufficient and, therefore, it is not possible to compare the results from different authors. Sometimes the growth of monocrystalline samples is necessary. This is often more time-consuming than for pure metals due to the different properties of each compound. Most intermetallics are brittle which makes the preparation of diffusion samples without cracks and surface defects difficult. Serial sectioning techniques, which work very well for ductile materials, —like lathe and microtome sectioning— are usually not applicable to intermetallics.

Furthermore, one should keep in mind that intermetallics form a numerous and manifold group of materials. Intermetallics comprise a greater variety of crystal structures than metallic elements. According to the strength and type of bonding, intermetallics can be grouped traditionally—although not completely unambiguously—into various classes. The most important classes are the Zintl phases, the Hume-Rothery phases and the size-factor compounds. Laves-phases are the best known size-factor compounds which comprise several hundred compounds. Intermetallics crystallize in structures with ordered atom distributions in which atoms are preferentially surrounded by unlike atoms. Some intermetallics are ordered up to the melting temperature, others undergo order-disorder transitions in which an almost random arrangement of atoms is stable at high temperatures. Such transitions occur, for example, between the β' and β phases in the Cu-Zn system or in FeCo. We know intermetallic phases with wide phase fields and others which exist as line compounds. Examples for both can even be found in the same binary alloy system: The Laves phase in the Co-Nb system (approximate composition Co_2Nb) exists over a composition range of about 5 at.%, whereas the phase Co_7Nb_2 is a line compound. Some intermetallics occur for certain stoichiometric compositions, others are observed for off-stoichiometric compositions only. Some phases compensate off-stoichiometry by vacancies others by antisite atoms. As a consequence of this variety and the unsatisfactory data situation the physical understanding of diffusion in intermetallics in terms of defect structure and atomic diffusion mechanisms is by far not

as complete as for metallic elements.

Considering this complex situation, it is clear that this overview will have to concentrate on some aspects of diffusion in intermetallics. The scope of the paper is as follows: We restrict ourselves to binary intermetallics. In Section II we will remind the reader of some of the more frequently encountered structures of binary intermetallics. We will also discuss implications of the lattice geometry for the diffusion behaviour. The various diffusion phenomena in binary systems like self-diffusion, foreign atom diffusion, interdiffusion in single-phase and multiphase diffusion couples will be considered in Section III and illustrated by recent examples from our laboratory. The Darken-Manning equation is sometimes used to correlate the tracer self-diffusivities of the constituents and the interdiffusion coefficient. We will discuss limitations of this procedure. Sections IV to VIII are devoted mainly to self-diffusion, which is the most basic diffusion process in solid matter anyway. Diffusion data for intermetallic compounds with B2-, L1_2 -, D0_3 -, D0_{19} -, L1_0 - and Laves-type structures will be reviewed. Relevant factors for self-diffusion in intermetallics like the crystal structure, the state of order and disorder, the temperature and composition dependence of diffusion will be illustrated by results from the literature and from our laboratory. In a few cases we will also consider information from the diffusion of selected foreign atoms. In the present context this is of particular interest when no appropriate tracer isotopes for the study of self-diffusion of (one) alloy constituent are available. Then it may be useful to consider diffusion of suitable foreign elements which reasonably well simulate self-diffusion.

It is well established that in pure metals or solid solution alloys diffusion occurs by the random motion of thermal vacancies⁽¹⁷⁾⁽¹⁸⁾. In intermetallics, however, random vacancy motion would disrupt the equilibrium ordered arrangement of atoms on lattice sites. Therefore, a physical understanding of diffusion in intermetallics must replace the concept of random vacancy motion by more sophisticated jump sequences. Our present understanding of atomic mechanisms of selfdiffusion in the various structures will be discussed.

II. Frequent Structures of Intermetallics—Some Geometrical Implications for Diffusion

1. Structures

Many intermetallics with the approximate composition AB crystallize in the B2 structure (see Fig. 1) also known as CsCl structure. Examples are (Fe, Co, Ni)Al, CoGa, PdIn, AuZn and AuCd. In the completely ordered state, A atoms occupy one cubic primitive sublattice and B atoms the other. This means that each A atom is surrounded by 8 B atoms on nearest neighbour (NN) sites and vice versa. If the A and B atoms are distributed at random, a body-centered cubic (bcc) structure (also denoted as A2 structure) is obtained. There are compounds with order-disorder transitions between B2- and

Fig. 1 Intermetallic crystal structures derived from the bcc lattice. B2 structure: In completely ordered AB compounds A (B) atoms occupy the sublattice of open (full) circles. D0₃ structure: In completely ordered A₂B compounds A (B) atoms occupy the sublattice of open and shadowed (full) circles.

A2 structures. The critical temperature of this transition depends on the ordering energy. Examples for compounds which undergo an order-disorder transition are CuZn and FeCo. Compounds with higher ordering energies are ordered up to the melting temperature.

Diffusion of the components is strongly influenced by the state of order. In a completely ordered compound random vacancy motion by NN jumps would destroy the order. By contrast, vacancy motion which is restricted to the sublattice of each constituent retains the order. It is well-known that self-diffusion in ionic crystals like CsCl occurs by sublattice vacancy motion⁽¹⁷⁾. Cation vacancies exchange their sites with cations and anion vacancies exchange their sites with anions only. Obviously, this requires that the atomic jump length is larger than the NN distance. Such jumps are favoured by the very high ordering energies in ionic crystals. It appears that in B2 intermetallics due to their relatively low ordering energies NN jumps are predominant⁽¹¹⁾. Then the necessity to maintain thermodynamic equilibrium between disordering and ordering jumps in the crystal leads to a coupling between the mass flows and hence between the diffusivities of the two atomic species⁽¹⁹⁾. In the literature also several subtle vacancy paths based on NN jumps have been proposed which satisfy this requirement by restoring the order during a jump sequence of an individual vacancy. These mechanisms include the six-jump cycle mechanism⁽²⁰⁾, the triple defect mechanism⁽²¹⁾ and the antistructure bridge mechanism⁽²²⁾, which will be discussed in some detail in Section IV.4. These mechanisms involve the formation of one or several antisite atoms as intermediate steps. Because diffusion is mediated by vacancies which interchange their sites both with A and B atoms, the diffusivities of both constituents, D_A^* and D_B^* , are not independent. The ratio D_A^*/D_B^* will be bound between certain limits.

Fig. 2 Intermetallic crystal structures derived from the fcc lattice. L1₂ structure: In completely ordered A₃B compounds A (B) atoms occupy the sublattice of open (full) circles. L1₀ structure: In the completely ordered AB compound A (B) atoms occupy the sublattice of open (closed) circles.

Several intermetallics with the approximate composition A₃B crystallize in the D0₃ structure (see Fig. 1), also denoted as Fe₃Si-type structure. It can be considered as an ordered structure derived from the bcc lattice. D0₃ order is observed for example in Fe₃Si and Fe₃Al (below about 825 K) and for some high-temperature phases. The sublattice of the majority component A is interconnected by NN bonds, whereas for the sublattice of the minority component B this is not the case. Thus the A component can diffuse within its own sublattice via NN jumps mediated by vacancies (jump vector: $(\sqrt{3}/2)a\langle 111 \rangle$). This is not possible for the B component. If B atoms migrate within their own sublattice their jump vector $(\sqrt{2}a\langle 110 \rangle)$ corresponds to a third nearest neighbour jump with respect to the bcc unit cell. An alternative are NN jumps which then create B antisite defects in the A sublattice. Both options are very likely associated with higher activation enthalpies for diffusion of B atoms as compared to A atoms.

Structures which can be derived from the face centered cubic (fcc) lattice like the L1₂ structure (Cu₃Au-type) and the L1₀ structure (CuAu-type) are illustrated in Fig. 2. Ni₃Al crystallizes in the L1₂ structure. With respect to its physical properties Ni₃Al is one of the best known and most studied intermetallic phases because it has been used already for long time as a particle strengthening phase in the so-called superalloys. The titanium aluminide TiAl—often designated as the γ phase of the Ti–Al system—crystallizes in the L1₀ structure. Because of the particular stacking of the atom planes, the L1₀ structure is no longer cubic but (slightly) tetragonally distorted.

The ordered hexagonal D0₁₉ structure (Ni₃Sn-type), which occurs at the (approximate) composition A₃B, is shown in Fig. 3. It is closely related to the hexagonal close-packed (hcp) lattice. For example the titanium aluminide Ti₃Al—also designated as α_2 -phase of the Ti–Al system—crystallizes in this structure. Their low densities and their promising high-temperature strength have made both titanium aluminides very attractive for materials developments (see, e.g., Refs. (4)(23)). In L1₂ and D0₁₉ compounds (composition A₃B) each A atom is sur-

Fig. 3 Structure of $D0_{19}$ intermetallics—an ordered structure in the hcp lattice. In completely ordered A_3B compounds A (B) atoms occupy the sublattice of open (full and shadowed) circles. A complete hexagonal cell is shown. For reasons of clarity B sites are shown as full circles only within the primitive cell.

Fig. 4 Cubic Laves-phase also designated as C15 structure (Cu_2Mg -type). In completely ordered AB_2 compounds A (B) atoms occupy the sublattice of open (full) circles.

rounded by 8 A atoms and 4 B atoms on NN sites. In contrast to this situation a B atom faces only A atoms on surrounding NN sites. This implies that similar to the $D0_3$ structure the sublattice of the majority component A is interconnected by NN bonds, whereas for the sublattice of the minority component B this is not the case. Vacancy motion which is restricted to the majority sublattice may promote diffusion of A atoms. However, diffusion of B atoms either requires jump lengths larger than the NN-distance or—if it is promoted by NN jumps of vacancies—the formation of antisite defects. The activation energy for either of these two possibilities is very likely higher than the activation energy for a NN jump in the majority sublattice.

The Laves phases with an approximate composition A_2B form a very large group of intermetallics. They crystallize in the hexagonal C14 structure, the cubic C15 structure and the dihexagonal C36 structure^{(24)–(26)}. These structures are topologically close-packed and belong to the family of the Frank-Kasper phases. The stability of the three crystal structures is controlled by both the atomic size ratio of the two atomic species and by the valence electron concentration. Deviations from the stoichiometric composition are accommodated primarily by antisite atoms⁽¹⁾. Only the cubic Laves structure (Cu_2Mg -type) is illustrated in Fig. 4. Very little is known about diffusion

in Laves phases. We will summarize the few available data and present some new results for Co_2Nb which crystallizes in the cubic C15 structure.

2. The Cu_3Au rule

The Cu_3Au rule^{(35)–(37)} provides a first approximation for an understanding of the self-diffusion behaviour in some intermetallic compounds. The rule states that in some compounds of type A_mB_n , where the ratio m/n is greater than 2, the majority element diffuses faster, in some cases even much faster, than the minority element:

$$D_A^* > D_B^*. \quad (1)$$

The inventors of this rule do not claim that it is universally valid. It is only applicable to compounds in which diffusion occurs via vacancies. Hägg phases like, *e.g.*, Fe_3C , where one of the two elements is sufficiently small to occupy interstitial sites in a matrix composed of the other element, must be excluded. For the reasons already discussed above A_3B intermetallics with $L1_2$ or $D0_3$ structure are expected to fulfill the ‘ Cu_3Au ’ rule. One would also expect that $D0_{19}$ compounds satisfy this rule since this structure is the hexagonal analogue to the $L1_2$ structure.

Self-diffusion data of both constituents are necessary to test this rule. Such data are unfortunately quite sparse for intermetallics. We will discuss below two very recent studies concerning the $L1_2$ compound Ni_3Ge and the $D0_3$ phase Fe_3Si . According to the authors knowledge—apart from an older study on the $D0_3$ phase Cu_3Sn —these are the only investigations in which the diffusion of both constituents has been studied. We shall see that eq. (1) is indeed fulfilled in these cases. However, for the technologically important compound Ni_3Al there are experimental hints that the validity of the rule is questionable.

III. Various Diffusion Phenomena in Binary Systems—Remarks on Experimental Techniques and Theoretical Concepts

1. Self-diffusion

When in a binary alloy (or compound) A_xB_{1-x} diffusion of A (or B) atoms is studied, one speaks about self-diffusion. Self-diffusion is the most basic diffusion process in solid matter. Studies of self-diffusion utilize tiny amounts of tracer atoms A^* (or B^*). In most experiments tracers are marked by their radioactivity. The isotopic mass of an enriched natural isotope has also been used as tag for tracer atoms. The so-called tracer method—illustrated in Fig. 5—is the most accurate technique for solid state diffusion studies⁽²⁷⁾. A thin layer of the tracer is usually deposited onto a flat surface of the diffusion sample. Sometimes the tracer is ion-implanted as a thin layer below the sample surface in order to overcome disturbing surface oxide hold-up and solubility problems⁽³⁰⁾. If the deposited layer is thin compared with the mean diffusion length, $\sqrt{D^*t}$, the distribution after a diffusion anneal is described by the thin-film solution of

Fig. 5 Schematic illustration of the tracer method: The major steps—deposition of the tracer, diffusion anneal, serial sectioning and evaluation of the penetration profile—are indicated.

Fig. 6 Penetration profiles of the radioisotope ^{59}Fe in Fe_3Si obtained by grinder sectioning. Solid lines represent fits of the thin film solution of Fick's second law to the data points.

Fick's second law

$$c(x, t) = \frac{N}{\sqrt{\pi D^* t}} \exp\left(-\frac{x^2}{4D^* t}\right). \quad (2)$$

Here $c(x, t)$ denotes the tracer concentration at a distance x from the surface after diffusion time t , and N the number of tracer atoms deposited per unit area. D^* is the tracer self-diffusion coefficient at temperature T . The concentration-depth profile is usually determined by serial sectioning of the sample and subsequent determination of the tracer concentration per section. If radioactive tracers are used, the specific activity per section (count rate normalized by the section weight) is proportional to the tracer concentration. The count rate is conveniently determined by an appropriate counting facility (γ - or β -counting, depending on the isotope). A plot of the logarithm of the specific activity versus the penetration distance squared according to eq. (2) should be linear if bulk diffusion is the dominating diffusion process. Its slope equals $-1/(4D^*t)$, from which the tracer diffusivity D^* is obtained. Since tiny amounts of tracer can be used in such an experiment the composition of the sample will not be influenced by the tracer. In this way self-

diffusion is studied in a (practically) homogeneous material[†]. As an example Fig. 6 shows penetration profiles of the radioisotope ^{59}Fe in the intermetallic Fe_3Si ⁽³¹⁾. Diffusivities in Fe_3Si obtained from such profiles will be discussed in Section VI. For average diffusion lengths of at least several micrometers mechanical techniques are appropriate for serial sectioning of diffusion samples (for a review see, *e.g.*, Ref. (27)). For many intermetallics due to their brittleness the only applicable mechanical technique is grinding. Sectioning in the case of Fig. 6 was done on a precision parallel grinder with special abrasive foil. The grinding device was specially designed for radiotracer diffusion studies of brittle materials and constructed in the workshop of our laboratory.

Diffusion studies at lower temperatures require the measurement of very small diffusivities. Serial sectioning of radiotracer diffusion profiles with mean penetration depths ($\sqrt{D^*t}$) in the micrometer or sub-micrometer range is possible using sputtering techniques⁽²⁷⁾. An apparatus for ion—beam—sputtering of diffusion samples recently designed at our laboratory is described in Ref. (33). Examples for penetration profiles of ^{59}Fe in the intermetallic Fe_3Al obtained with this device are displayed in Fig. 7 according to Ref. (34). As can be seen from Fig. 8, diffusivities of ^{59}Fe in Fe_3Al obtained from the sputter-sectioned (closed symbols) and from grinder-sectioned penetration profiles (open symbols) cover a range of diffusivities of about 9 orders of magnitude. Using sputter sectioning the measurements could be extended to temperatures below the critical temperature of the B2/D0₃ order transition of Fe_3Al .

As already mentioned above, enriched stable isotopes can be used as tracers as well. Then secondary ion mass spectrometry (SIMS) is an appropriate technique for depth profiling. Contrary to radiotracer experiments, in studies with a stable isotope the natural abundance of this isotope limits the concentration range of the diffusion profile. Highly enriched isotopes should be used. A beautiful example of this technique can be found in a recent study of Ni self-diffusion in the intermetallic compound Ni_3Al . In this case a highly enriched stable ^{64}Ni isotope was used Ref. (32).

Table 1 compiles binary intermetallics with the structures described in Section II for which self-diffusion data are available in the literature. We will consider self-diffusion in Sections IV to VIII in more detail.

2. Impurity diffusion

When in a binary alloy (or compound) A_xB_{1-x} the diffusion of foreign atoms X is studied, one speaks about

[†] There is no chemical gradient in the sample, only a concentration gradient of the tracer atoms. The latter usually have an isotopic mass which is slightly different from that of the matrix atoms. Differences between the isotopic masses lead to isotope effects in diffusion. These are an interesting phenomena by itself (see, *e.g.*, Refs. (28) and (29)). A part from hydrogen diffusion, which is not the topic of the present paper, the differences between diffusivities of two different isotopes of the same element are a few percent only. Isotope effects will not be considered further in this paper.

Fig. 7 Penetration profiles of the radioisotope ^{59}Fe in Fe_3Al obtained by sputter sectioning. Solid lines represent fits of the thin film solution of Fick's second law to the data points.

Fig. 8 Arrhenius diagram of ^{59}Fe diffusion in Fe_3Al : open symbols— D -values from grinder sectioning; full symbols— D -values from sputter sectioning. The temperatures of the $\text{D0}_3 \leftrightarrow \text{B2}$ and $\text{B2} \leftrightarrow \text{A2}$ phase transitions of Fe_3Al are also indicated.

Table 1 Compilation of some binary intermetallics. The components for which tracer self-diffusion data are available in the literature (see references) are underlined.

Structure	Intermetallic
B2	<u>CuZn</u> ⁽³⁸⁾⁽³⁹⁾ , <u>AuCd</u> ⁽⁴²⁾⁽⁴³⁾ , <u>AuZn</u> ⁽⁴⁴⁾⁽⁴⁵⁾⁽⁴⁶⁾
	<u>CoGa</u> ⁽²¹⁾ , <u>PdIn</u> ⁽⁴⁸⁾ , <u>FeCo</u> ⁽⁴⁰⁾
	<u>NiAl</u> ⁽⁴⁹⁾⁽⁵⁰⁾ , <u>Fe(Al)</u> ⁽⁵¹⁾⁽³⁴⁾ , <u>AgMg</u> ⁽⁵²⁾⁽⁵³⁾⁽⁵⁴⁾ , <u>NiGa</u> ⁽⁴⁷⁾
L1 ₂	<u>Ni₃Al</u> ⁽⁵⁰⁾⁽⁵⁵⁾⁽⁵⁶⁾⁽⁵⁷⁾⁽³²⁾ , <u>Co₃Ti</u> ⁽⁵⁸⁾ , <u>Ni₃Ge</u> ⁽⁵⁹⁾ , <u>Pt₃Mn</u> ⁽⁶⁰⁾
	<u>Cu₃Au</u> (disordered) ⁽⁶²⁾
D0 ₃	<u>Fe₃Si(Ge)</u> ⁽³¹⁾ , <u>Cu₃Sn</u> ⁽⁶⁵⁾⁽⁶⁶⁾⁽⁶⁷⁾ , <u>Cu₃Sb</u> ⁽⁶⁸⁾
	<u>Ni₃Sb</u> ⁽⁶⁹⁾ , <u>Fe₃Al</u> ⁽³⁴⁾
L1 ₀	<u>TiAl</u> ⁽⁷³⁾
D0 ₁₉	<u>Ti₃Al</u> ⁽⁷⁴⁾
Laves-phases	
cubic:	<u>Co₂Nb</u> ⁽⁷⁰⁾
hexagonal:	<u>Zn₂Mg</u> ⁽⁷¹⁾ , <u>Fe₂Ti</u> ⁽⁷²⁾

impurity diffusion. Diffusion of foreign elements is a phenomenon which is of interest in itself. As already mentioned in this overview, we will mainly concentrate on self-diffusion. However, in a few cases we will also consider diffusion of selected foreign atoms. In the context of the present overview impurity diffusion is of particular interest when no appropriate tracer isotopes for the study of self-diffusion of an alloy constituent are available. As already mentioned examples are aluminium and silicon: The radioisotope ^{26}Al is extremely expensive and ^{31}Si is too short-lived (half-life: 2.6 h) for routine experiments. In such cases it may be expedient to consider, *e.g.*, the diffusion of isoelectronic (homologous) tracer atoms and/or tracer atoms with similar atomic radii. Below we will present results of ^{71}Ge in Fe_3Si which replaces the ^{31}Si tracer. A further example is ^{114}In diffusion in Ni_3Al which was studied instead of Al diffusion. A crucial question in this context is whether foreign atoms X substitute onto the appropriate sublattice. For L1₂ structure $\text{Ni}_3\text{Al-X}$ and $\text{Al}_3\text{Ti-X}$ alloys the available evidence for the site preference of foreign elements determined by various experimental techniques has been collected in Table 1 of a recent review paper by Kogachi⁽⁷⁵⁾. Unfortunately, no site preference determination seems to be available for In in Ni_3Al .

3. Interdiffusion (chemical diffusion)

A diffusion coefficient which is measured in a sample in which a chemical composition gradient prevails is denoted as chemical or interdiffusion coefficient $\bar{D}$. The experimental procedure of an interdiffusion study is schematically illustrated in Fig. 9. A diffusion couple which consists of two homogeneous, homo-phase alloys with different compositions (A_xB_{1-x} and A_yB_{1-y}) but within the same phase field of the phase diagram is formed. The interdiffusion profile after a diffusion anneal is measured, *e.g.*, by electron microprobe analysis. An example of a single-phase interdiffusion profile resulting

Fig. 9 Schematic illustration of a single-phase interdiffusion experiment. The original interface (Kirkendall plane) is marked by inert markers. The position of the Matano plane (x_M) is also indicated.

from a $\text{Al}_{50}\text{Ni}_{50}$ – $\text{Al}_{43}\text{Ni}_{57}$ couple is shown in Fig. 10⁽⁹⁷⁾. Boltzmann-Matano analysis, which is based on Boltzmann's transformation of Fick's second law⁽⁷⁶⁾ and a procedure suggested by the Japanese scientist Matano⁽⁷⁷⁾, is employed to evaluate—in general concentration dependent—interdiffusion coefficients from a measured profile according to

$$\tilde{D}(c^*) = \left(2t \frac{\partial c}{\partial x} \Big|_{x^*} \right)^{-1} \int_{c^-}^{c^*} (x_M - x) dc. \quad (3)$$

Here t is the time of the diffusion anneal and x the position. In eq. (3) x_M denotes the position of the so-called Matano plane, which is defined by

$$\int_{c^-}^{c^+} (x_M - x) dc = 0. \quad (4)$$

c^- and c^+ refer to the initial compositions of the two starting alloys (see Fig. 9). To deduce $\tilde{D}$ one determines the Matano interface first. Afterwards, the area corresponding to the integral in eq. (3) and the slope of the tangent to the $c(x)$ curve at the concentration c^* are calculated (see Fig. 9). This procedure is repeated for vari-

ous choices of c^* . In this way $\tilde{D}$ values are obtained for various compositions (see Fig. 10 as an example Ref. (97))[†].

According to an analysis of interdiffusion given by Darken⁽⁸⁵⁾ and slightly generalized by Manning^{(86)–(88)} the interdiffusion coefficient $\tilde{D}$ is related to the tracer self-diffusion coefficients D_A^* and D_B^* of the components of a homogeneous alloy (or compound) via^{††}

$$\tilde{D} = (X_A D_B^* + X_B D_A^*) \Phi R. \quad (5)$$

Here X_A and X_B denote the mole fractions of the components, Φ is the thermodynamic factor, and R is the so-called 'vacancy wind factor'. Using a classical result from thermodynamics of binary systems, the thermodynamic factor can be written as Ref. (17)

$$\Phi = \frac{X_A X_B}{RT} \frac{d^2 G}{dX_A^2} = 1 + \frac{\partial \ln \gamma_i}{\partial \ln X_i} \quad (6)$$

where G denotes Gibbs free energy and γ_i the coefficient of the thermodynamic activity of species i ($= A$ or B). According to the Gibbs-Duhem relation for binary systems the thermodynamic factor is identical for both species. The thermodynamic factor is unity for ideal solutions. It is larger than unity for phases with negative deviations from ideality and smaller than unity in the opposite case. Negative deviations are expected for systems with order. Therefore, thermodynamic factors of intermetallic compounds are often larger, sometimes even considerably larger than unity due to the attractive interaction between the constituents of the intermetallic phase. As a consequence, interdiffusion coefficients are often larger than the bracket term in eq. (5), which contains a weighted average of the tracer diffusivities. Activation enthalpies of interdiffusion are often smaller than those for tracer diffusion due to the temperature variation of the thermodynamic factor.

Sometimes eq. (5) is used in the literature to convert tracer diffusion coefficients to interdiffusion coefficients and vice versa. Obviously such a procedure needs information about Φ and R . Measurements of the thermodynamic activity are necessary to get Φ . Data for some intermetallics can be found, e.g., in Ref. (90). In some cases theoretically calculated values for the thermodynamic factor, e.g., from Calphad calculations of phase diagrams are available. A relatively frequent use of eq. (5) is to calculate one unknown diffusion coefficient of the set $(\tilde{D}, D_A^*, D_B^*)$ from two measured coefficients.

[†] In eq. (3) volume changes have been neglected for reasons of simplicity. In general the total volume of the sample will change in the course of interdiffusion. This is the case if the molar volume V_m of the alloy (or compound) deviates from Vegard's rule. Then eq. (3) needs some modification. The case of non-constant total volume was treated by Sauer and Freise⁽⁷⁸⁾ and later on by den Broeder⁽⁷⁹⁾, in review articles (e.g., in Ref. (80)) and in several textbooks⁽¹⁷⁾⁽¹⁸⁾⁽⁸¹⁾. The interdiffusion coefficient can be obtained from the measured composition profile using

$$\tilde{D}(c^*) = \left(2t \frac{\partial c}{\partial x} \Big|_{x^*} \right)^{-1} V_m(c^*) \left[(1 - c^*) \int_{-\infty}^{x^*} \frac{c}{V_m} dx + c^* \int_{x^*}^{+\infty} \frac{1 - c}{V_m} dx \right].$$

Provided that the molar volume is known as a function of composition, eq. (2) can be used to determine $\tilde{D}$.

^{††} For systems with volume changes during the interdiffusion process eq. (5) must be replaced by

$$\tilde{D} = (c_A \bar{V}_A D_B^* + c_B \bar{V}_B D_A^*) \Phi R$$

where c_i and $\bar{V}_i$ denote concentration and partial molar volume of species i , respectively.

Fig. 10 Composition profile of a $\text{Al}_{50}\text{Ni}_{50}$ - $\text{Al}_{43}\text{Ni}_{57}$ diffusion couple after an anneal of 17.67 h at 1473 K (left). Interdiffusion coefficients $\bar{D}$ obtained from Boltzmann-Matano analysis (right).

Such a procedure may be helpful to get information which is difficult to obtain by other means, *e.g.*, if no appropriate tracer isotope is available to study self-diffusion of one of the components. However, one should also be aware of the fact that in the derivation of eq. (5) several assumptions were made which makes this procedure somehow questionable:

- The concentration of vacancies is assumed to be in equilibrium during the entire interdiffusion process. Equivalent to this assumption is that the gradient of the chemical potential of vacancies (μ_v) and its contribution to atomic fluxes is neglected. However, deviations from vacancy equilibrium have been observed during atomic transport when electric or thermal gradients act as driving forces. It has been claimed that chemical gradients during a single phase interdiffusion can also cause deviations from vacancy equilibrium⁽⁸⁹⁾.
- The formation of Kirkendall pores in interdiffusion couples is disregarded in eq. (5).
- The 'vacancy wind factor' accounts for the fact that in a substitutional alloy unequal diffusion fluxes of atoms are compensated by a net flux of vacancies. In some papers eq. (5) is used with $R=1$. Such an approximation neglects coupling between the diffusion fluxes and correlation effects. An atomistic model is necessary to deduce an explicit expression for R . Within the framework of Manning's 'random alloy model' the expression⁽⁸⁶⁾⁽⁸⁷⁾

$$R = 1 + 2 \frac{1-f_0}{f_0} \frac{X_A X_B (D_A^* - D_B^*)^2}{(X_A D_A^* + X_B D_B^*)(X_A D_B^* + X_B D_A^*)} \quad (7)$$

has been derived (see, *e.g.*, Refs. (17) and (18)). f_0 denotes the correlation factor for self-diffusion by the vacancy mechanism in the pure matrix with the given structure. f_0 equals 0.781 or 0.727 for an fcc or a bcc structure respectively. $R-1$ expresses the existence of the 'vacancy wind', which results from the coupling of the fluxes of A and B atoms, via the flux of vacancies. Depending on the ratio D_A^*/D_B^* the possible range of R -values for the random alloy model is limited:

$$1 \leq R \leq 1 + \frac{1-f_0}{f_0}. \quad (8)$$

To the authors knowledge, however, for none of the intermetallic structures discussed in Section II theoretical expressions for the vacancy wind factors are available. Therefore, one should keep in mind that the limits given in eq. (8) are not necessarily correct for ordered compounds.

Shimozaki *et al.*⁽⁹¹⁾ have tried to check experimentally the validity of eq. (5) for B2-type ordered AuZn. Tracer diffusion coefficients D_{Zn}^* and D_{Au}^* ⁽⁴⁴⁾ and activity data of Zn in AuZn⁽⁹⁴⁾ are known from literature. From the latter the thermodynamic factor can be deduced, which has a pronounced maximum (≈ 40) at the stoichiometric composition. Shimozaki *et al.* use eqs. (5) and (7) to calculate $\bar{D}$ and find good agreement with their experimental interdiffusion coefficients. This may indicate that R -values close to unity obtained from eq. (7) are probably not unrealistic. However, in view of the relatively large values of the thermodynamic factor deviations from eq. (7) might have been overlooked.

- During interdiffusion of atoms with different atomic volumes internal stresses arise. Internal stresses provide additional driving forces for diffusion currents. The problem of stress contribution to the diffusion currents is an interesting but delicate question of diffusion theory which cannot be considered in detail here. For the present purpose it may suffice to point out that in the analysis of interdiffusion by Darken and Manning leading to eq. (5) the contribution of stresses has been neglected. The Darken-Manning equation is only applicable if a complete relaxation of stresses has occurred. The influence of stresses on diffusion are particular important for thin film diffusion couples and for couples with 'closed geometry'. Some aspects of the influence of stresses on diffusion can be found in a recent review⁽⁹²⁾ and in the Proceedings of a recent workshop on 'Diffusion and Stresses'⁽⁹³⁾.

4. Multi-phase diffusion (reaction diffusion)

The formation and growth of intermetallic compounds in diffusion couples is already an old subject of physical metallurgy and material science (see, *e.g.*, Refs. (80) and (81)). The experimental procedure is schematically illustrated in the upper part of Fig. 11. A diffusion couple is formed from the two elements A and B or from two compounds A_xB_{1-x} and A_yB_{1-y} . Depending on the phase diagram of the system interdiffusion will give rise to the formation of one or several intermetallic layers. A hypothetical phase diagram (containing only one intermetallic compound) and a concentration profile resulting from interdiffusion is illustrated in the lower part of Fig. 11. This phenomenon is usually denoted as multi-phase diffusion; this name emphasizes the diffusional aspect of the whole process. However, there is also the aspect of a chemical reaction between the atomic species at the phase boundaries. The overall kinetics of such a process can be either

Fig. 11 Schematic illustration of a multi-phase diffusion experiment. Upper part: Diffusion couple before and after a diffusion anneal. Lower part: Interrelation between a hypothetical phase diagram and the interdiffusion profile.

governed by diffusion across the growing product phase(s) or by reaction(s) occurring at the interfaces. In the first case the process is denoted to be 'diffusion controlled'; in the second case it is denoted to be 'reaction controlled'. In general the kinetics of formation and growth of intermetallics will be the result of both processes. For this phenomenon the name reaction (reactive) diffusion has been suggested⁽⁸²⁾⁽⁸³⁾. In very thin layers diffusion processes proceed very fast and therefore the reaction is in the interface-reaction controlled regime. However, during progress of reaction diffusion the layer thickness increases. Then diffusion of the reacting species needs more and more time. Finally, diffusion processes determine the overall kinetics.

(1) Diffusion-controlled growth of intermetallic layers

When during the intermixing process local thermodynamic equilibrium is maintained and the process is 'diffusion controlled', the thickness Δx_j of the growing intermetallic layer of phase j in a binary system obeys a parabolic growth law

$$\Delta x_j^2 = 2k_j t. \quad (9)$$

In a classical treatment Kidson⁽⁹⁵⁾ has shown that growth constants k_j have the following meaning:

$$k_j = 2 \left\{ \left[\frac{(\tilde{D}K)_{kj} - (\tilde{D}K)_{jk}}{C_{jk} - C_{kj}} \right] - \left[\frac{(\tilde{D}K)_{ji} - (\tilde{D}K)_{ij}}{C_{ij} - C_{ji}} \right] \right\}^2. \quad (10)$$

C_{ij} denotes the equilibrium composition on the i -side of an i/j -interface, $\tilde{D}_{ij}$ the interdiffusion coefficient in the i -phase near the i/j -interface, and K_{ij} is the composition gradient in the i -phase near the i/j -interface in a diagram of concentration versus $x/\sqrt{t}$. As already mentioned, in the derivation of eq. (10) any explicit influence of interface processes like phase nucleation, atomic transfer across the interface and the creation and/or annihilation of point defects at the interfaces has been disregarded. This is only justified for long enough diffusion times when the growth process is completely diffusion controlled⁽⁸²⁾⁽⁸⁴⁾.

We consider two recent examples from our laboratory in which 'diffusion controlled growth' was observed: A first example concerns multiphase diffusion in the system Ni-Al⁽⁹⁷⁾. Apart from the primary and terminal solid solutions five intermetallic compounds are present in the phase diagram of Ni-Al: Al_3Ni , Al_3Ni_2 , AlNi , Al_3Ni_5 and Ni_3Al . Figure 12 shows an optical micrograph of a diffusion couple of pure Al and Ni after a diffusion anneal of 48 h at 823 K. Layers of the Al-rich intermetallic compounds Al_3Ni and Al_3Ni_2 are clearly visible. Their compositions can be identified in the profile across the diffusion zone measured by electron microprobe analysis also shown in Fig. 12. The layer thicknesses of Ni-rich compounds—at the relatively low temperature of the diffusion anneal—are too small to be detectable in Fig. 12. As can be seen from Fig. 13 the compound Al_3Ni_2 indeed shows parabolic growth. Its growth constant $k_{\text{Al}_3\text{Ni}_2}$ is thermally activated (Fig. 14) and described by

$$k_{\text{Al}_3\text{Ni}_2} = 3.7 \cdot 10^{-6} \exp \left(-\frac{126 \text{ kJ mol}^{-1}}{RT} \right) \text{ m}^2 \text{ s}^{-1}. \quad (11)$$

Figure 15 shows the growth kinetics of an intermetallic layer of Co_2Nb in a multi-phase diffusion couple between Co and Nb (see also Refs. (98)–(100)). Three intermetallic compounds— CoNb , Co_2Nb and Co_7Nb_2 —can be found in the Co-Nb phase diagram. The layer thickness of the cubic Laves-phase Co_2Nb follows eq. (9) for each temperature investigated. Figure 16 shows the temperature dependences of the growth constants of Co_2Nb and Co_7Nb_2 . An Arrhenius type temperature dependence is observed in the case of Co_2Nb and given by

$$k_{\text{Co}_2\text{Nb}} = 1.0 \cdot 10^{-6} \exp \left(-\frac{212 \text{ kJ mol}^{-1}}{RT} \right) \text{ m}^2 \text{ s}^{-1}. \quad (12)$$

According to eq. (10) is applicable, growth constants have a complex meaning. They depend on diffusivities in the bordering layers as well as on the diffusivity of the growing phase, on the concentration gradients on both sides of the interfaces, and on the (in general temperature dependent) solubility limits of the phases. If one deduces an activation enthalpy for the growth process it has a complex meaning as well. Its value is usually not identical with the activation enthalpy of interdiffusion in the growing layer. The assignment of an activation enthalpy to the growth of an intermetallic layer is at most only an average of several more fundamental activation enthalpies. If a linear Arrhenius plot is observed for the growth constant, this is useful empirically. However, it indicates either that one of the terms dominates over the others, or that the activation enthalpies are similar to each other⁽⁹⁵⁾. In addition (see below), growth constants may be influenced by mass transport along diffusion short circuits like grain boundaries in the growing layer. In the case of Co_7Nb_2 Fig. 16 shows that the temperature dependence of the growth constant cannot be described by an Arrhenius relation in the entire temperature range. The decrease of the growth constant above 1300 K is attributed to the fact that the Co_7Nb_2 -phase vanishes at high

Fig. 12 Optical micrograph of Al-Ni diffusion couple after a diffusion anneal of 48 h at 823 K (left). Composition profile obtained by electron microprobe analysis (right).

Fig. 13 Parabolic growth of the intermetallic compound Al_3Ni_2 in Al-Ni diffusion couples.

temperatures, as can be seen from the phase diagram of Co-Nb (for details see Refs. (98)–(100)).

These examples show that sometimes the growth of intermetallic layer is indeed 'diffusion controlled'. However, many experimental investigations about growth of intermetallic phases in diffusion couples where eq. (9) is violated can be found in the literature (see, *e.g.*, Ref. (80) for a review).

(2) Interdiffusion coefficients from multi-phase diffusion studies

Multi-phase diffusion (reaction diffusion) experiments

Fig. 14 Growth constant of intermetallic layers Al_3Ni_2 in Al-Ni diffusion couples.

in connection with electron microprobe analysis can also be used to determine interdiffusion coefficients of intermetallics. An obvious experimental advantage of such a procedure is that it is not necessary to produce the compound as single phase material prior to the diffusion experiment which can be very tedious and time-con-

Fig. 15 Parabolic growth of the cubic Laves-phase Co_2Nb in diffusion couples of Co and Nb.

Fig. 16 Growth constants of layers of the cubic Laves-phase Co_2Nb and of Co_7Nb_2 in diffusion couples of Co and Nb.

suming. In a solid-state diffusion-reaction experiment the compound will grow during the experiment. The Boltzmann-Matano analysis of concentration depth profiles described in Section III.3 is applicable not only to single-phase interdiffusion but also to multi-phase diffusion profiles. However, one should be aware that interdiffusion coefficients determined from multi-phase diffusion couples ($\tilde{D}_{\text{multi-phase}}$) are often larger than diffusion coefficients ($\tilde{D}_{\text{single-phase}}$) determined in single-phase interdiffusion experiments

$$\tilde{D}_{\text{multi-phase}} \geq \tilde{D}_{\text{single-phase}} \quad (13)$$

for several reasons:

- Phase boundaries are inevitably present in a multi-phase diffusion sample. The existence of these boundaries provides an additional reason for deviations from the thermal equilibrium of vacancies which then will influence the diffusion fluxes of atoms. For example, it is well known from semiconductor technology that thermal oxidation of silicon enhances the diffusion of, *e.g.*, phosphorus and boron. Driven by the chemical reaction between the growing oxide layer and the Si substrate, point defects are injected into the Si crystal. The associated supersaturation of point defects leads to the phenomenon of oxidation-enhanced diffusion (for a recent review see, *e.g.*, Ref. (96)). Point defect injection during oxidation of metals has also been observed (see Ref. (83) for references). Similar effects as during the growth of oxide layers presumably occur during the growth of intermetallic layers as well.
- Even if intermetallic layers grow according to the parabolic growth law of eq. (9) this does not necessarily mean that their growth kinetics is controlled by bulk diffusion. Intermetallic layers growing in a multi-phase diffusion couple are polycrystalline. A simple but frequently observed microstructure is columnar growth of grains with their long axis perpendicular to the layer. In this case the transport through the layer is not governed by the lattice diffusion coefficient alone but by an effective diffusivity⁽⁸²⁾⁽⁸³⁾

$$\tilde{D}_{\text{eff}} = \tilde{D} + 2D_{\text{gb}}\delta/d. \quad (14)$$

Here D_{gb} denotes the grain-boundary diffusivity, d the average grain diameter and δ the grain-boundary width. Independent of the details of the microstructure of a growing intermetallic layer, grain boundaries may significantly contribute to the atomic transport through this layer.

- The formation of intermetallic phases in a multi-phase diffusion couple is accompanied by volume changes. Only if a complete relaxation of internal stresses caused by the volume change can occur during the experiment, the influence of stresses can be neglected (see also the discussion in Section III.3).

Section IV has shown that self-diffusion of the components is the most basic diffusion process in an intermetallic compound. Its understanding on an atomistic basis is very fundamental to the whole field. The phenomena of single-phase interdiffusion or even more so of multi-phase diffusion are very important from practical viewpoints. However, these phenomena are clearly more complex and an atomistic interpretation is less straightforward than for self-diffusion measured by tracer methods in a homogeneous compound. In the rest of the paper we will mainly concentrate on self-diffusion.

IV. Self-Diffusion in B2 Intermetallics

1. Survey

It is obvious from Table 1 that the B2 phases are the most thoroughly investigated intermetallics. Figure 17

shows an Arrhenius diagram with self-diffusivities of all the B2 intermetallics listed in Table 1. The compounds $\text{AuCd}^{(42)}$, $\text{AuZn}^{(44)}$, $\text{AgMg}^{(52)(54)}$, $\text{CoGa}^{(21)}$, $\text{NiGa}^{(47)}$, $\text{FeAl}^{(51)}$, $\text{NiAl}^{(49)(50)}$, and $\text{PdIn}^{(48)}$ have also been investigated for several compositions. Clearly, the composition dependence of the diffusivities is a further important piece of information. For reasons of clarity, however, only data for the composition closest to the stoichiometric one have been included in Fig. 17.

Several B2 phases are so-called IIIB-VIIIA compounds which are composed of a group VIIIB metal (Co, Fe, Ni, Pd,...) and a group IIIA metal (Al, Ga, In,...). B2 phases composed of a noble metal (Cu, Ag, Au) and a divalent metal (Mg, Zn, Cd) form a second class. The only exception is FeCo, which does not fit into this scheme. Figure 17 shows a remarkable feature of self-diffusion in B2 phases. Let us consider self-diffusion in CuZn as an example (see also Fig. 18). We recognize that Zn diffuses only slightly faster than Cu. The ratio $D_{\text{Zn}}^*/D_{\text{Cu}}^*$ never exceeds 2.37⁽³⁸⁾. For equiatomic FeCo the ratio $D_{\text{Fe}}^*/D_{\text{Co}}^*$ always is close to unity⁽⁴⁰⁾. A similar 'coupling' between the diffusivities of the components can be observed in Fig. 17 for practically all B2 compounds for which both constituents have been investigated. In some cases the bounds for D_A^*/D_B^* are somewhat wider than in the cases of CuZn and FeCo. However, the difference between the diffusivities usually lies within less than one order of magnitude. This 'coupling' between the diffusivities of the components indicates that the diffusion of both atomic species is somehow mediated by the same defect.

2. Defect structure

The basic lattice defects that can occur in a binary compound like a B2 phase are the following[†]:

1. A atoms on the B sublattice (also denoted as A antisite defects A_B),
2. B atoms on the A sublattice (also denoted as B antisite defects B_A),
3. vacancies on the A sublattice (V_A),
4. vacancies on the B sublattice (V_B).

In which concentrations these defects occur, depends on the magnitude of their formation energies, on the composition of the compound, and on temperature. According to the dominating type of lattice defect, B2 phases have been divided in the literature into two categories—compounds with substitutional (or antisite) disorder and compounds with triple-defect disorder (see, *e.g.*, Refs. (9) and (101)):

Compounds in which antisite defects are considered to be the dominating defects are denoted as systems with *substitutional or antisite disorder*. For example, CuZn and FeCo belong to this category. Above the critical temperature of the order-disorder transition the long-range order parameter is zero. Then A and B atoms can be found with equal probabilities on both sublattices. Upon approaching the critical temperature from the B2 ordered

Fig. 17 Self-diffusion in B2 structure intermetallics.

Fig. 18 Self-diffusion of Cu and Zn in CuZn (β - and β' -brass).

region the concentration of antisite defects becomes so high that the distinction of two sublattices loses its meaning. The very rapid self-diffusion in CuZn (see Fig. 17) points to considerably higher thermal vacancy concentrations than in metallic elements. It has been reported already more than a decade ago that thermal vacancies are easily formed in this compound⁽¹⁰²⁾. This is supported by

[†] The occurrence of self-interstitials, which is unlikely under thermal equilibrium conditions, has been disregarded.

positron annihilation studies on CuZn⁽¹⁰³⁾⁽⁶⁾⁽¹⁰⁴⁾. These studies showed that no structural vacancies are formed on both sides of the stoichiometry. The onset temperature where an appreciable positron trapping at thermal vacancies occurs is very low (about 370 K in Cu₅₁Zn₄₉). The pertaining vacancy formation enthalpy is only 0.42 eV.

A second category of B2 compounds forms predominantly antisite defects (A_B) on the A-rich side of the stoichiometric composition whereas vacancies in the A sublattice (V_A) dominate on the B-rich side. This type of disorder has been denoted as *triple-defect disorder*⁽¹⁰⁵⁾. At the stoichiometric composition three defects—namely two V_A and one A_B —must exist simultaneously in order to maintain the stoichiometric ratio. It has been suggested⁽¹⁰¹⁾ that triple-defect disorder occurs in B2 structure intermetallics composed of group VIIIB and group IIIA metals. In this context it may be helpful to recall that group VIIIB elements often have smaller atomic radii than group IIIA elements.

Extensive studies of the vacancy content of the compounds CoGa⁽¹¹⁷⁾⁽¹¹⁸⁾ and NiGa⁽¹¹⁹⁾ have been performed by measuring thermal expansion of macroscopic length and lattice parameter. The experiments revealed a large amount of vacancies (up to 5% near the melting temperature) for nearly all compositions. These high vacancy concentrations may be attributed to the coupling between antisite disorder and vacancy formation. For each A_B antisite defect two vacancies V_A are formed.

The concept of triple-defect disorder receives also some theoretical support from very recent ab initio calculations: The defect structure of Fe_xAl_{1-x} has been investigated by Mayer *et al.*⁽¹¹³⁾ within the framework of a grand canonical formalism. The atomic defects considered in this study were Fe antisite atoms on the Al sublattice (Fe_{Al}), Al antisite atoms on the Fe sublattice (Al_{Fe}), vacancies on the Fe sublattice (V_{Fe}) and vacancies on the Al sublattice (V_{Al}). The defect energy parameters were calculated using density functional theory in the local-density approximation⁽¹¹⁴⁾. The calculations were performed for supercells with 16 and 32 atoms and still depend slightly on the size of the supercell. The result for 16 atoms supercell calculation is displayed in Fig. 19. Due to the high defect formation energy the concentration of V_{Al} is always very low. For Fe-rich alloys Fe_{Al} is the dominant defect. On the Al-rich side V_{Fe} dominates and for the stoichiometric composition the concentration of V_{Fe} is about twice the concentration of Fe_{Al} [†]. Interestingly enough, this strongly resembles the behaviour of a system with triple-defect disorder, apart from the non-negligible contribution of Al_{Fe} for the Al-rich compound. However, at the stoichiometric composition the calculated concentrations are considerably smaller than V_{Fe} concentrations deduced from positron life time studies⁽¹¹⁵⁾. A possible

Fig. 19 Calculated concentrations of defects in FeAl according to Mayer *et al.*

reason for this discrepancy could be the neglect of formation entropies in the calculations⁽¹¹³⁾.

3. The influence of the order-disorder transition

The pioneering work of Kuper *et al.*⁽³⁸⁾ on CuZn is shown in Fig. 18. Below the order-disorder transition (at about 741 K) the compound shows B2 order. At high temperatures the disordered bcc structure is formed. The influence of the order-disorder transition on the diffusion behaviour of both components is visible as a change in slope of the Arrhenius plot which starts already somewhat above the transition temperature. The activation enthalpies obey the inequality

$$Q_{\text{ordered}} > Q_{\text{disordered}} \quad (15)$$

Diffusion in CuZn is a remarkably fast process. For example, the diffusivity in a bcc metallic element near the melting temperature is typically only between 10^{-11} and 10^{-12} m² s⁻¹. The occurrence of order impedes the diffusion of both components in similar way. As already mentioned above the ratio D_{Zn}^*/D_{Cu}^* never exceeds 2.37. The change in the slope of the Arrhenius diagram could be reproduced at least qualitatively in computer simulations using NN interaction models. An interesting result of these computer simulations (performed for an equiatomic compound) was that the change in slope is mainly due to the temperature dependence of the correlation factor, which has an almost constant value in the disordered region but decreases strongly with decreasing temperature below the order-disorder transition. For details the reader is referred to the work of Bakker *et al.*⁽⁹⁾⁽⁴¹⁾. Another system which undergoes a transition from B2 order to a disordered bcc phase near 1000 K is equiatomic FeCo, for which diffusion of both components was studied by Fishman *et al.*⁽⁴⁰⁾. Like in the case of CuZn the occurrence of B2 order impedes the diffusivities of both components (see Fig. 17). Measurements of the isotope effect of Fe diffusion⁽⁴⁰⁾ show a decrease with decreasing temperature below the order-disorder transition temperature,

[†] A simple-minded argument may help to remember why the formation energy of V_{Al} is significantly higher than that of V_{Fe} : V_{Al} has eight Fe atoms as nearest neighbours; it is somehow 'similar' to a vacancy in metallic Fe. By contrast, V_{Fe} has only Al atoms as nearest neighbours. The formation energy of a vacancy in pure Fe is considerably higher than in pure Al.

which has been attributed to the decreasing correlation factor[†].

4. Diffusion mechanisms

When atomic diffusion takes place by random interchanges between vacancies and nearest neighbour atoms, in a highly B2 ordered compound migrating vacancies would leave traces of antisite defects (disordered regions) behind. In order to maintain thermodynamic equilibrium in the compound the disordered regions must be compensated during the diffusion process.

An ingenious mechanism (HME mechanism) which fulfils this condition for the path of an individual vacancy was proposed by Huntington (see Elcock and McCombie⁽¹⁰⁷⁾). On the basis of the assumption that the unit process of diffusion in B2 phases is the interchange between a vacancy and a nearest neighbour atom, it was suggested that the principal diffusion mechanism is a closed cycle of six successive vacancy-atom exchanges. The pertaining vacancy path is illustrated in Fig. 20. A vacancy starting, e.g., from the sublattice of A atoms (α sublattice) performs a sequence of 6 correlated NN jumps, which only temporarily increases the energy. During the first 3 jumps antisite atoms are created which are annihilated again in the next three steps. After the cycle has been completed the vacancy is residing on the α sublattice again; the A atom is shifted by one lattice parameter; B atoms I and II have exchanged their positions; the order is restored microscopically. Vacancy 'excursions' developing into other jump configurations are energetically less favourable and are thus usually retraced. Actually the HME mechanism is the simplest low energy path of a vacancy in a highly ordered B2 structure. From Fig. 20 it is obvious that for the HME mechanism a relatively close coupling between the diffusivities of A and B atoms must exist. Bakker suggested the following formula for the ratio of the diffusivities⁽⁹⁾

$$\frac{D_A^*}{D_B^*} = \frac{C_V^\alpha \omega_6^\alpha + 2C_V^\beta \omega_6^\beta}{2C_V^\alpha \omega_6^\alpha + C_V^\beta \omega_6^\beta}, \quad (16)$$

Fig. 20 Vacancy path of the six-jump cycle (HME-mechanism) in the B2 structure.

[†] Unfortunately, this argument has a missing link. In simple situations like vacancy diffusion in cubic metals the isotope effect parameter E is related to the correlation factor f via

$$E = f\Delta K,$$

where ΔK is the so-called kinetic energy factor. However, in more complex situations like diffusion via the mechanisms discussed below no such simple relation between the isotope effect parameter and the correlation factor exists⁽⁹⁾⁽¹²³⁾.

where $C_V^\alpha(C_V^\beta)$ denote the vacancy fractions on the $\alpha(\beta)$ sublattice and $\omega_6^\alpha(\omega_6^\beta)$ the frequencies with which a vacancy, starting on the $\alpha(\beta)$ sublattice, completes a full jump cycle. From eq. (16) the diffusivities of both species are bound between the following limits:

$$0.5 < D_A^*/D_B^* < 2. \quad (17)$$

Several early theoretical studies have been devoted to the six-jump cycle mechanism⁽¹⁰⁸⁾⁽¹⁰⁶⁾⁽¹⁰⁹⁾. Since this work has already been critically discussed in the excellent review of Bakker⁽⁹⁾ we will not repeat this discussion here. More recently a detailed theoretical analysis of the six-jump vacancy cycle in the B2 type lattice was published by Koiwa and coworkers^{(110)–(112)}. Explicit expressions for the diffusion coefficients of A and B atoms in terms of the vacancy jumps including correlation effects have been derived and a comprehensive discussion of the isotope effect was given. Furthermore the average vacancy jump frequencies $\omega_6^{\alpha,\beta}$ have been expressed analytically in terms of individual vacancy jump frequencies. Although the expressions are complicated, their temperature dependences could be approximated by single Arrhenius equations with apparent activation enthalpies. Koiwa and coworkers also pointed out that eqs. (16) and (17) have some shortcomings because correlation effects were not considered and because the fact that two types of vacancy jump cycles (denoted as 100- and 110-cycles) exist was not taken into account properly. Equation (16) has to be replaced by the expression⁽¹¹¹⁾

$$\frac{D_A^*}{D_B^*} = \frac{f_A^\alpha C_V^\alpha \omega_6^\alpha (2 - P_{100}^\alpha) + 2f_A^\beta C_V^\beta \omega_6^\beta \left(1 + \frac{1}{3} P_{100}^\beta\right)}{2f_B^\alpha C_V^\alpha \omega_6^\alpha \left(1 + \frac{1}{3} P_{100}^\alpha\right) + f_B^\beta C_V^\beta \omega_6^\beta (2 - P_{100}^\beta)} \quad (18)$$

where α and β indicate that the relevant quantity is related to a vacancy belonging to the respective sublattice. For example, f_A^α denotes the correlation factor of an A atom promoted by the six-jump cycle of α vacancies and P_{100}^α is the probability for an 100-displacement of an atom caused by an α vacancy. The new expression for the bounds of the ratio D_A^*/D_B^* which replaces eq. (17) is

$$0.4917 < D_A^*/D_B^* < 2.034. \quad (19)$$

Although this inequality is not much different numerically from the one given by Bakker⁽⁹⁾, the derivation in Ref. (111) is mathematically on a sound basis.

In early experimental studies it was felt that a critical appraisal of the applicability of this mechanism can be made on the basis of a comparative study of both components in a stoichiometric compound. For example, studies of self-diffusion of ¹¹⁰Ag and ²⁸Mg in stoichiometric AgMg have been reported⁽⁵³⁾ (see also Fig. 17). The ratio D_{Mg}^*/D_{Ag}^* increases with temperature from 0.65 to about 1.25. It is, however, clearly within the bounds of eq. (19). The authors of the experimental work on AgMg⁽⁵³⁾ explained their results by the HME mechanism. This and similar results for other B2 phases which revealed a close coupling between D_A^* and D_B^* (see, e.g., Fig. 18)

Fig. 21 Vacancy path of the 'antistructure bridge (ASB) mechanism' in the B2 structure.

were taken as evidence for the HME mechanism.

Some of the intermetallics listed in Table 1 (CuZn, FeCo, AgMg) are systems which exhibit substitutional disorder in which the excess component is accommodated as antisite atoms on the 'wrong' sublattice. Whereas CuZn and FeCo have been investigated for (nearly) equiatomic composition only, Ag diffusion in AgMg was also studied as a function of composition⁽⁵⁴⁾⁽⁵²⁾. The isothermal values of the Ag diffusion coefficient showed a minimum near the equiatomic composition. For an ordered phase with substitutional disorder the vacancy path illustrated in Fig. 21 constitutes an additional low energy sequence of vacancy jumps. This vacancy path has been named by Chang and coworkers⁽²²⁾ as antistructure-bridge (ASB) mechanism. Clearly the ASB mechanism becomes more important at deviations from stoichiometry. A superposition of the HME and the ASB mechanisms is in principle able to account for the compositional dependence of the diffusivity in compounds with substitutional disorder.

Already in 1969 Kikuchi and Sato⁽¹⁹⁾ presented their path-probability method which can also be used for systems with incomplete order and for off-stoichiometric compositions. They argued that the applicability of the HME mechanism is limited and that it should be restricted to stoichiometric compounds in which the degree of order is extremely high. A more general treatment has to be based on the application of the principles of statistical mechanics. The whole crystal must be considered in thermodynamic equilibrium. From this point of view it is not necessary to restore order during each unit process of a vacancy, because the disorder caused by one atomic jump can be compensated by a reverse jump somewhere else in the crystal. Kikuchi and Sato were also able to demonstrate that their theoretical calculations agree well with experimental results for AgMg^{(52)–(54)}. This indicates that a decisive conclusion on the diffusion mechanism may be difficult on the basis of diffusivity measurements alone.

One of the most comprehensive diffusion studies on a IIIA–VIIIB compound was performed by Stolwijk *et al.*⁽²¹⁾ on CoGa. The diffusion of both components was measured over a wide temperature range and for various compositions on both sides of stoichiometry. The Arrhenius diagrams for diffusion show upward curvature for each component and were analysed in terms of a superposition of two Arrhenius equations. The lower activation energy of Co diffusion was attributed to Co NN jumps to the Ga sublattice[†]. The higher activation enthalpy of Ga diffusion was attributed to Ga jumps within

its own sublattice. Interesting features of the results are that the higher activation enthalpy of Co diffusion equals the lower activation enthalpy of Ga diffusion and that the associated pre-exponential factors are also similar. Stolwijk *et al.*⁽²¹⁾ invented an ingenious diffusion mechanism denoted as triple-defect mechanism which comprises coupled diffusion of Co and Ga. This mechanism also fits to the triple defect disorder of CoGa. According to

two vacancies on both sublattices form a triple defect. As illustrated in Fig. 21 diffusion via (bound) triple defects implies that Co atoms can migrate between the two sublattices, whereas Ga atoms jump within the Ga sublattice only^{††}. Since diffusion of Co and Ga atoms is mediated by the same defect the diffusion coefficients of both components are again 'coupled'. The ratio of the triple-defect mediated diffusivities is given by⁽¹¹⁶⁾

$$\frac{D_A^*}{D_B^*} = \frac{f_A \omega_A^{12}}{f_B 2\omega_B^{11}}, \quad (21)$$

where ω_B^{11} denotes the jump frequency of B atoms within the β sublattice and $\omega_A^{12}(\omega_A^{21})$ the jump frequency of A atoms from an $\alpha(\beta)$ into a $\beta(\alpha)$ lattice site (see Fig. 22). f_A and f_B are correlation factors which can also be expressed in terms of $\omega_A^{12}/2\omega_B^{11}$. Differences in the jump frequencies between A and B atoms are smoothed out in the diffusion coefficients and associated activation enthalpies by the correlation factors. The diffusivities of both species are bound between the following limits⁽²¹⁾⁽¹¹⁶⁾:

$$1/13.3 < D_A^*/D_B^* < 13.3. \quad (22)$$

The experimental ratios D_{Co}^*/D_{Ga}^* lie within the range of eq. (22) but clearly outside the limits that are allowed for the HME mechanism⁽²¹⁾.

Fig. 22 Jump sequence during triple-defect migration in a two dimensional analogue of the B2 structure.

5. Elementary diffusion jumps studied by Mößbauer spectroscopy

A brief account of diffusion studies with Mößbauer spectroscopy (MBS) and its application to intermetallic compounds can be found in a recent review by Vogl⁽¹²⁰⁾. A great advantage of MBS lies in the fact that it is a microscopic method which can be used to unravel details of the atomic jump processes which are not directly accessible to tracer diffusion studies. The elementary process

[†] This mechanism has been later termed ASB mechanism⁽²²⁾.

^{††} The latter process is facilitated by the presence of the other vacancy of the vacancy pair.

of Fe diffusion in B2 ordered Fe–Al intermetallics was investigated in Refs. (121)(122) by measuring the angular dependence of the Mößbauer line broadening relative to oriented Fe–Al monocrystals (Fe contents 50.5, 55 and 66 at.%). Within the time window of Mößbauer spectroscopy the net displacements of Fe atoms occurring during a unit diffusion event can be determined. For Fe–Al close to equiatomic stoichiometry the authors conclude that Fe atoms are displaced to different neighbour sites on the Fe sublattice. The net displacement can be understood as a combination of jump into a nearest neighbour vacancy—leading to a short-time occupation of an anti-structure site on the Al sublattice—and a jump into a vacancy back on the Fe sublattice. With increasing Fe concentration and at sufficiently high temperatures the residence time of the Fe atom on the anti-structure site increases until it approaches the residence time on the Fe sublattice⁽¹²²⁾. Diffusion coefficients of ⁵⁷Fe in Fe–Al have also been deduced from the Mößbauer spectra. It is well known that Mößbauer spectroscopy is not a routine method for the determination of diffusion coefficients over a wide temperature range because is limited to a fairly narrow temperature window, within which the average jump time of atoms is comparable with the life time of the Mößbauer level. Nevertheless, the agreement between diffusivities determined from the Mößbauer experiments⁽¹²²⁾ with available tracer data⁽⁵¹⁾ is quite good.

V. Diffusion in L₁₂ Intermetallics

As already mentioned in Section III.1 the structure of the L₁₂ (or Cu₃Au) intermetallics can be derived from the fcc lattice. These compounds form a (narrow) homogeneity range on both sides of the stoichiometric composition. The off-stoichiometry is compensated by antisite atoms on each sublattice⁽¹⁾. Tracer self-diffusion data for L₁₂ intermetallics are compiled in Fig. 23. The only L₁₂ compound for which reliable self-diffusion data for both components are available is Ni₃Ge. According to Yasuda *et al.*⁽¹³⁾ diffusion of the majority component Ni is significantly faster than that of the minority component Ge. The Cu₃Au rule, introduced in Section II.2 is fulfilled, in the case of Ni₃Ge. For Cu₃Au itself the rule could so far not be verified by tracer diffusion experiments. Because of the low ordering temperature (663 K) of Cu₃Au and the associated very low diffusivities no tracer diffusion data for this material are available in the ordered state. Au diffusion in a Cu₃Au alloy has been investigated by Benci *et al.*⁽⁶²⁾ and is shown in Fig. 23. However, these data refer to the disordered state. The same is true for the work of Heumann and Rottwinkel⁽⁶³⁾ who studied Au and Cu diffusion at 1133 K for Cu–Au solid solution alloys of various compositions including the Cu₃Au alloy. Cu diffuses slightly faster than Au (see also Ref. (16)).

As already mentioned in Section II the group of L₁₂ intermetallics includes the technologically important compound Ni₃Al. As a precipitate phase Ni₃Al is responsible for the particle hardening of commercial Ni base ‘superal-

Fig. 23 Self-diffusion in L₁₂ structure intermetallics.

loys’. There are several investigations of Ni self-diffusion in Ni₃Al^{(32)(50)(55)–(57)} which more or less coincide at high temperatures. An enhanced diffusivity at lower temperatures was reported by Hoshino *et al.*⁽⁵⁷⁾ and ascribed to structural vacancies. However, this ‘low temperature enhancement’ has not been confirmed in very recent measurements of Frank *et al.*⁽³²⁾. Very likely the ‘enhancement’ found in Ref. (57) is not an intrinsic property of Ni₃Al but rather due to an underestimated influence of grain boundary diffusion. In Fig. 24 Ni self-diffusion in Ni₃Al according to Ref. (32) is shown together with self-diffusion in pure Ni⁽¹²⁶⁾⁽¹²⁷⁾. Ni diffusion is slightly slower in Ni₃Al than in pure Ni. Taking into account the difference between the melting temperatures of Ni₃Al (1911 K) and Ni (1726 K) the diffusivities would almost coincide in a normalized temperature scale. This suggests that Ni diffusion in Ni₃Al—like in pure Ni—occurs via NN jumps which are mediated by thermal vacancies. This conclusion is supported by positron annihilation studies by Schaefer and coworkers⁽¹²⁵⁾⁽¹²⁴⁾, where independent of composition, no constitutional vacancies have been detected in Ni₃Al. Furthermore, Schaefer *et al.*⁽¹²⁵⁾ deduce thermal vacancy concentrations on the Ni sublattice of Ni₃Al, which are similar to the values in pure fcc Ni. There is also one investigation of Al diffusion in Ni₃Al⁽⁵¹⁾ with the (nowadays) very expensive radioisotope ²⁶Al. As already pointed out by Wever⁽¹¹⁾ this measurement is doubtful and could have been strongly influenced by grain-boundary diffusion. Therefore, the Al data⁽⁵¹⁾ carry a question mark in Fig. 23.

The results for diffusion of ¹¹⁴In in Ni₃Al obtained by Shi and Wever⁽¹²⁸⁾⁽¹²⁹⁾ are also displayed in Fig. 24. Indium like Al is a group IIIA element and one might expect that its diffusion behaviour is not too dissimilar from that of Al itself provided that In atoms substitute for Al

Fig. 24 Diffusion in Ni₃Al and self-diffusion in fcc Ni.

atoms in Ni₃Al. Unfortunately, no information about the preferred site of In atoms in Ni₃Al appears to be available⁽⁷⁵⁾. Nevertheless, Fig. 24 casts some doubt on the validity of the Cu₃Au rule for Ni₃Al. The activation enthalpy of In diffusion (3.77 eV)[†] is slightly higher than that of Ni diffusion in Ni₃Al (3.14 eV). Calculations with the 'embedded atom method' yield values for the formation energy of Al antisite defects in the Al sublattice between 0.54 eV⁽¹³⁰⁾ and 0.46 eV⁽¹³¹⁾. These numbers suggest that In (and Al) atoms invade the Ni sublattice and diffuse via Ni vacancies.

VI. Diffusion in D0₃ Intermetallics

As already mentioned in Section II the D0₃ structure (Fig. 1) is an ordered structure within the bcc lattice. Considering the fully ordered state—that is possible only for the stoichiometric composition A₇₅B₂₅—the lattice sites marked by open and shadowed circles in Fig. 1 are occupied by A atoms while the B atoms are located in the sublattice marked by full circles. The sublattice occupied by A atoms is interconnected by nearest neighbour distances. Therefore, the majority component in this structure is able to migrate via NN jumps on its own sublattice without disturbing the order. By contrast, B atoms are surrounded by A atoms. For the minority component diffusion is possible either by third nearest neighbour jumps or by formation of antisite atoms.

Diffusion of the radiotracers ⁵⁹Fe and ⁷¹Ge in the D0₃ phase Fe₃Si has been studied over wide temperature ranges and for three different alloy compositions by

Fig. 25 Self-diffusion in D0₃ structure intermetallics on a homologous temperature scale.

Gude and Mehrer^{(31)††}. The major results are summarized in the Arrhenius diagram of Fig. 25 on a homologous temperature scale. The most salient features of diffusion in Fe₃Si are the following: Fe diffusion in D0₃-ordered Fe₃Si alloys is faster than in disordered iron-silicon alloys (not shown in Fig. 25). Its activation enthalpy is comparatively low. The diffusivity of Fe increases significantly with increasing Si content. It is fastest in the nearly stoichiometric compound. Diffusion of Ge is by orders of magnitude slower than Fe diffusion and only weakly dependent on the alloy composition. In one experiment with the short-lived ³¹Si tracer it was demonstrated that Si and Ge diffuse at very similar rates. A discussion of the diffusion results together with further information from the literature about Fe₃Si led to the following major conclusions⁽³¹⁾: Considering the large differences between the diffusivities of Fe and the Si substitute Ge, it appears that the diffusion of the two components in D0₃ ordered Fe₃Si is 'decoupled'. Self-diffusion in Fe₃Si fulfills the Cu₃Au rule of Section II.2. The elementary jump process of Fe in Fe₃Si has been investigated using ⁵⁷Fe Mößbauer spectroscopy by Sepiol and Vogl⁽¹³²⁾⁽¹³³⁾. From the linewidth of the quasielastic line measured in various directions on single crystals the atomic jump mechanism has been deduced. These studies support a simple mechanism for Fe diffusion by exchange of Fe atoms with NN vacancies on the Fe sublattice in Fe₃Si. In addition, high thermal vacancy concentrations and low vacancy formation enthalpies were observed in positron annihilation studies by Kümmerle *et al.*⁽⁶⁴⁾. This fits to the fast Fe diffusion ob-

[†] The lowest data point, which deviates considerably from the Arrhenius line, has been omitted for the determination of this activation enthalpy.

^{††} Some penetration profiles of ⁵⁹Fe in Fe₃Si from this work have already been shown in Section III.1 to illustrate radiotracer work in conjunction with grinder sectioning.

served for Fe_3Si . The composition dependence of Fe diffusion is mainly due to the composition dependence of the thermal vacancy concentration: the ratios of the vacancy concentrations and the Fe diffusion coefficients for different alloy compositions are almost the same. With increasing Fe surplus, both the Fe diffusivity and the thermal vacancy concentration decrease. For the minority component of Fe_3Si comparatively little is known about the diffusion mechanism. From the structure it is clear that either antisite atoms are involved or the elementary jump is further than to nearest neighbour sites. As Ge diffusion does not seem to profit from the higher vacancy concentration in nearly stoichiometric alloys, a Si sublattice mechanism is more likely.

Tracer experiments on three other D0_3 phases are reported in the literature: The diffusion of ^{63}Ni in Ni_3Sb in alloys with 28.3, 27.1, 26.3 and 25.0 at.% Sb Heumann and Stürer⁽⁶⁹⁾ and the diffusion of ^{64}Cu in Cu_3Sb with 21, 25 and 29 at.% Sb has been investigated by Heumann *et al.*⁽⁶⁸⁾. Only for Cu_3Sn with 16.6, 18.0, 19.8 and 20.2 at.% Sn diffusion experiments for both components have been carried out^{(65)–(67)}. All intermetallic phases mentioned above are high temperature phases which exist in relatively narrow temperature regions only. Except for Cu_3Sb these phases exist in off-stoichiometry only. The information about diffusion in D0_3 phases is presented in Fig. 25 along with the diffusion data of the already discussed phase Fe_3Si . Different alloy compositions within the same diffusion system are represented by the same line type. The arrows indicate the variation of the diffusion coefficients with increasing content of minority atoms. In all cases the diffusion of the majority component in the D0_3 phases is surprisingly fast and the corresponding activation enthalpy very low. A higher concentration of minority atoms leads to faster diffusion and to a lower activation enthalpy of the majority component. The diffusion of the minority component, investigated for Cu_3Sn and Fe_3Si only, is clearly slower than that of the majority component. The minority atoms seem to diffuse somewhat slower when their concentration is raised.

VII. Diffusion in the D0_{19} - and L1_0 -Type Compounds of the Ti–Al System

Titanium aluminides are technologically important because of their potential as high-temperature structural materials with high strength-to-weight ratio. Of considerable interest are two intermetallic compounds in the Ti–Al system, namely Ti_3Al and TiAl . Two-phase alloys of these two intermetallics, which usually form lamellar microstructures, show improved ductility with respect to the homogeneous compounds. Until recently only interdiffusion data for titanium aluminides were available from multi-phase diffusion couples⁽¹³⁴⁾. However, these data are only partly qualified for a discussion of the underlying mechanisms (see the discussion in Section III.4). Until recently no diffusion data on homogeneous titanium aluminides (see, *e.g.*, Ref. (16)) were available. For-

tunately, this situation has changed in the meantime.

As already mentioned in Section III.1 the titanium aluminide Ti_3Al —often also designated as α_2 phase of the Ti–Al system—crystallizes in the D0_{19} structure, which is an ordered structure within the hcp lattice (see Fig. 3). It can be considered as the hexagonal analogue to the Cu_3Au (L1_2) structure. One therefore should expect that the ‘ Cu_3Au ’ rule should be applicable to Ti_3Al . Rüsing and Herzig⁽⁷⁴⁾ from our laboratory have studied ^{44}Ti tracer diffusion and chemical diffusion in Ti_3Al . The tracer diffusion results are summarized in Fig. 26. The Ti diffusivities are fairly low and similar to self-diffusion in $\alpha\text{-Ti}$ ⁽¹³⁵⁾. The Ti diffusivity in Ti_3Al is—on a homologous temperature scale—also comparable with the Ni diffusivity in L1_2 type intermetallic Ni_3Al . This can be seen from a comparison of Figs. 24 and 26 if one keeps in mind that the liquidus temperature of a Ti_3Al alloy is by about 200 K higher than that of Ni_3Al (1633 K). Furthermore, the Arrhenius parameters found in Ref. (74) are in line with the semiempirical rule of Brown and Ashby⁽¹³⁶⁾. Rüsing and Herzig also observed that there is practically no dependence of the Ti diffusivity on the composition (see Fig. 26), which indicates the absence of a significant contribution of constitutional vacancies to the diffusion process. From the D0_{19} structure it is also clear that Ti can diffuse via NN jumps in its own sublattice. Diffusion via thermal vacancies in the Ti sublattice is the most probable option for the atomic mechanism of Ti diffusion although direct information about thermal vacancies is lacking. In this context positron annihilation studies would be very desirable. Rüsing and Herzig also studied interdiffusion in the D0_{19} phase. Supposing the validity of Darken’s equation and using their ^{44}Ti diffusivities as well as values for the thermodynamic factor obtained

Fig. 26 Diffusion in intermetallic compounds Ti_3Al (α_2 phase) and TiAl (γ phase) of the Ti–Al system.

from Calphad-calculations they estimate values for the Al diffusivity that are by about a factor of three smaller than the Ti diffusivities. This result is in line with the Cu_3Au rule which suggests that Al as the minority component of Ti_3Al should be the slower diffuser.

As already mentioned in Section II the titanium aluminide TiAl —often designated as the γ phase of the Ti–Al system—crystallizes in the tetragonal L1_0 structure (CuAu type) shown in Fig. 2. Its tetragonal distortion is fairly small. The ratio of the lattice parameters c and a is only 1.015 at the stoichiometric composition.

Recently, two diffusion studies on γ TiAl have been published. The results are displayed in Fig. 26. Diffusion of ^{44}Ti was studied in our laboratory by Kroll *et al.*⁽⁷³⁾ (see also Ref. (100)). Since the L1_0 structure is closely related to the fcc structure the authors compared their results with the self-diffusivities of pure fcc metals and found that on a homologous temperature scale Ti diffusion in γ - TiAl lies within the fairly narrow ‘diffusion spectrum’ of fcc metals. This finding points to a diffusion mechanism in which Ti diffusion is mediated by thermal vacancies. This conclusion is strongly supported by a recent study of thermal vacancy formation in γ - TiAl by positron lifetime spectroscopy⁽¹³⁷⁾⁽¹²⁴⁾. An estimate of the concentration of thermal vacancies yields a value of $C_V(T_M) = 2.6 \times 10^{-4}$ at the melting temperature. Such values are also typical for thermal vacancy concentrations in pure fcc metals (see, e.g., Ref. (138)). Sprengel, Oikawa and Nakajima⁽¹³⁹⁾ very recently performed a single-phase interdiffusion study in γ - TiAl . No composition dependence of the interdiffusion coefficient was observed since the diffusion profiles could be fitted by complementary error functions. The temperature dependence of the interdiffusion coefficient almost coincides with that of the ^{44}Ti tracer diffusivities reported by Kroll *et al.* (see Fig. 26). Assuming the validity of Darken’s equation and using literature data for the thermodynamic factor⁽⁹⁰⁾, the authors conclude that the Al diffusivity ‘is of the same order as the Ti diffusivity or, at maximum, one and a half orders of magnitude smaller’. Considering the L1_0 structure an Al diffusivity which is of similar magnitude as the Ti diffusivity appears quite plausible.

Sometimes in discussions about diffusion in γ - TiAl it is argued that there should be a significant anisotropy of diffusion parallel and perpendicular to the tetragonal axis. This question could be clarified in future diffusion experiments on monocrystalline samples. The above mentioned experiments of Kroll *et al.*⁽⁷³⁾ were performed on polycrystals. However, in the author’s opinion such an anisotropy is very likely not pronounced, i.e., for two reasons: (i) In a macroscopic sample the Ti and Al layers will be interrupted by antiphase boundaries. (ii) Self-diffusion anisotropies in tetragonal or hexagonal metallic elements are well known. These anisotropies are fairly small⁽¹⁶⁾. For example, the ratio of self-diffusivities in pure indium parallel and perpendicular to its tetragonal axis is only slightly smaller than unity and the diffusivities differ by not more than 30 to 40%⁽¹⁴⁰⁾.

VIII. Diffusion in Laves-Phases

Laves phases are intermetallics with the approximate composition AB_2 . As already mentioned in Section II, 1 Laves phases constitute the most numerous group of intermetallic phases. The sublattice of the minority component is formed by the the larger A atoms. The majority sublattice is occupied by the smaller B atoms. Nowadays, several hundred Laves phase compounds are known (see, e.g., Refs. (142) and (141)). Laves phases crystallize in the cubic MgCu_2 -type structure (also denoted as C15 structure), in the hexagonal MgNi_2 -type structure (C36), and in the hexagonal MgZn_2 -type structure (C14). All three structures are topologically closely packed with average coordination numbers larger than 12⁽¹⁴²⁾. The cubic Laves-phase structure (see Fig. 4) consists of two interpenetrating cubic sublattices. The A sublattice is a diamond-type lattice. The distance between the four nearest neighbours sites in the A sublattice is $\sqrt{3}a/4$ of the cubic lattice parameter a . Sublattice B can be considered as a network of interconnected tetrahedrons in which each B atom has six nearest neighbours in the distance $\sqrt{2}a/4$. The interatomic distances are illustrated in Fig. 27. On the basis of the structure one might expect diffusion of the components in their own sublattices. On the other hand it is known that deviations from stoichiometry are usually compensated by antisite effects (for references see Ref. (1)).

Up to now there are only very few diffusion studies and even less defect studies on such compounds in the literature. Arrhenius plots for the few available data on self-diffusion in Laves compounds are shown in Fig. 28. Günzel *et al.*⁽⁷¹⁾ reported tracer diffusion data for ^{65}Zn in Zn_2Mg , which is a hexagonal C14 Laves compound. Tracer diffusion of ^{59}Fe in Fe_2Ti —another hexagonal C14 compound—was studied by Shinjaev⁽⁷²⁾. Very recent investigations on tracer diffusion of ^{57}Co in the cubic Laves phase Co_2Nb from our laboratory⁽⁷⁰⁾ are also included in Fig. 28. Unfortunately, a study of tracer self-diffusion of both components in the same Laves compound is still lacking.

The best studied Laves phase is Co_2Nb . Figure 29 shows an Arrhenius diagram of ^{57}Co tracer diffusion⁽⁷⁰⁾

Fig. 27 Arrangement of atoms in the (110) plane of a cubic Laves phase structure. In the completely ordered AB_2 structure A (B) atoms occupy open (full) sites.

Fig. 28 Self-diffusion in Laves phase intermetallics in homologous temperature scale.

Fig. 29 Diffusion in the cubic Laves phase Co_2Nb and in fcc Co.

and of interdiffusion data. The latter are obtained from multi-phase diffusion experiments^{(98)–(100)}. Self-diffusion in fcc Co⁽¹⁴³⁾, which occurs by thermal vacancies, is also indicated in Fig. 29 for comparison. As already discussed in Section III.4.(2) one should keep in mind that interdiffusion coefficients due to the influence of the ther-

modynamic factor, due to possible vacancy supersaturation effects and due to grain boundary enhancements are often larger than tracer diffusivities and the pertaining activation enthalpies often smaller than in tracer diffusion experiments on the same material. Saito and Beck⁽¹⁴⁴⁾ have performed a comparison of the X-ray density with gravimetrically measured densities for the Co-rich compounds of the Co–Nb system. Their measurements show that the homogeneity range of the Co_2Nb Laves phase is the result of the progressive occupation of Nb sites by Co atoms, and not the result of structural vacancies in the Nb sublattice. These findings of Saito and Beck⁽¹⁴⁴⁾, the values of the pre-exponential factor and the activation enthalpies for Co diffusion as well as the similarity of the diffusion behaviour to fcc cobalt are indications of a thermal vacancy mechanism in Co_2Nb .

Acknowledgements

The author would like to thank many coworkers (Dipl. Phys. M. Denking, Dipl. Phys. M. Eggersmann, Dr. Anja Gude, Dr. F. Wenwer, Dipl. Phys. U. Schöo, Dr. W. Sprengel (now at Iwate University)) and colleagues (Prof. Dr. Chr. Herzig, Dr. N. A. Stolwijk, Prof. Dr. E. Nembach) from the Institut für Metallforschung for discussions and cooperation over the years. He is also grateful to Prof. G. Vogl (Universität Wien) for helpful comments on the manuscript and to Prof. Dr. H. Nakajima (Iwate University) for information on self-diffusion in Ni_3Ge prior to publication. This work was partly supported by the Deutsche Forschungsgemeinschaft (projects Me 480/24 and Me 480/30).

REFERENCES

- (1) G. Sauthoff: *Intermetallics*, VCH Verlagsgesellschaft, Weinheim (1995).
- (2) J. H. Westbrook: *Structural Intermetallics*, ed. by R. Dariola, J. J. Lewndowski, C. T. Liu, P. L. Martin, D. B. Miracle, and M. V. Nathal, Warrendale, PA: TMS, (1993), p. 1.
- (3) N. S. Stoloff, R. G. Davies: *Progr. Mater. Sci.*, **13** (1966), 1.
- (4) M. Yamaguchi, Y. Umakoshi: *Progr. Mater. Sci.*, **34** (1990), 1.
- (5) J. H. Westbrook, R. L. Fleischer: *Intermetallic Compounds—Principles and Practice*, New York, John Wiley and Sons, (1994).
- (6) M. Yamaguchi and Y. Shirai: *Physical Metallurgy and Processing of Intermetallic Compounds*, ed. by N. S. Stoloff and K. Sikka, Chapman & Hall, New York, in press.
- (7) G. Sauthoff: *Diffusion in Ordered Alloys*, ed. by B. Fultz, R. W. Cahn, D. Gupta, TMS, EMPMD Monograph Series, (1993), p. 205.
- (8) H. Bakker: *Diffusion in Metals and Alloys*, ed. by F. J. Kedves and D. L. Beke, Trans. Tech. Publications, (1983), p. 189.
- (9) H. Bakker: *Diffusion in Crystalline Solids*, ed. by G. E. Murch and A. S. Nowick, Academic Press, (1984), p. 189.
- (10) H. Wever, J. Hünecke, G. Froberg: *Z. Metallkde.*, **80** (1989), 389.
- (11) H. Wever: *Defect and Diffusion Forum*, **83** (1992), 55.
- (12) H. Bakker, D. M. R. LoCascio: *Defect and Diffusion Forum*, **95–98** (1993), 803.
- (13) H. Yasuda, H. Nakajima, M. Koiwa: *Defect and Diffusion Forum*, **95–98** (1993), 823.
- (14) F. J. Kedves, D. L. Beke (Eds.): *DIMETA-88 Diffusion in Metals and Alloys*, Defect and Diffusion Forum, **66–69** (1989); Proc. of the Int. Conf. held at Balatonfüred (Hungary), 1988.
- (15) M. Koiwa, K. Hirano, H. Nakajima, T. Okada (Eds.): *Diffusion in Materials DIMAT-92*, Trans. Tech. Publications 1993, Proc.

- of the Int. Conf. on Diffusion in Materials held at Kyoto (Japan), 1992; Also: Defect and Diffusion Forum, **95-98** (1993).
- (16) H. Mehrer (Ed.): *Diffusion in Metals and Alloys*, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series Vol. III/26, Springer Verlag, (1990).
 - (17) J. Philibert: *Atom Movements—Diffusion and Mass Transport in Solids*, Les Editions de Physique, (1991).
 - (18) Th. Heumann: *Diffusion in Metallen*, Springer Verlag, Berlin (1992).
 - (19) R. Kikuchi and H. Sato: J. Phys. Chem. Sol., **51** (1969), 161.
 - (20) stated in: E. W. Elcock and C. W. McCombie: Phys. Rev., **109** (1958), 605.
 - (21) N. A. Stolwijk, M. van Gend and H. Bakker: Phil. Mag., **A 42** (1980), 783.
 - (22) C. R. Kao and Y. A. Chang: Intermetallics, **1** (1993), 237; C. R. Kao, S. Kim, Y. A. Chang: presented at the 'Workshop on Defects, Dynamics and Diffusion in Intermetallics' at Vienna, Austria, Sept. 1994.
 - (23) M. Yamaguchi: Mater. Sci. Technology, **8** (1992), 299.
 - (24) F. Laves: *Intermetallic Compounds*, ed. by J. H. Westbrook, New York, Wiley, (1977), p. 129.
 - (25) J. H. Wernick: *Intermetallic Compounds*, ed. by J. H. Westbrook, New York, Wiley, (1977), p. 1.
 - (26) J. D. Livingston: Phys. Status Solidi, (a) **131**, 415.
 - (27) S. J. Rothman: *Diffusion in Crystalline Solids*, ed. by G. E. Murch and A. S. Nowick, Academic Press, (1964), p. 1.
 - (28) N. L. Peterson: J. Nucl. Mat., **69/70** (1978), 3.
 - (29) H. Mehrer: J. Nucl. Mat., **69/70** (1978), 38.
 - (30) H. Mehrer: Phys. Stat. Sol., (a) **104** (1987), 247.
 - (31) A. Gude and H. Mehrer: Phil. Mag., in print.
 - (32) S. Frank, U. Södervall and Chr. Herzig: Phys. Status Solidi, (b) **191** (1995), 45.
 - (33) F. Wenwer, A. Gude, G. Rummel, M. Eggersmann, T. Zumkley N. A. Stolwijk and H. Mehrer: Meas. Sci. Technol., **7** (1996), 632.
 - (34) M. Eggersmann and H. Mehrer: to be published.
 - (35) F. M. d'Heurle and P. Gas: J. Mater. Res., **1** (1986), 205.
 - (36) F. M. d'Heurle and R. Ghez: Thin Solid Films, **215** (1992), 19 and 26.
 - (37) F. M. d'Heurle, P. Gas and J. Philibert: Solid State Phenomena, **41** (1995), 93.
 - (38) A. B. Kuper, D. Lazarus, J. R. Manning and C. T. Tomizuka: Phys. Rev., **104** (1956), 1536.
 - (39) N. L. Peterson and S. J. Rothman: Phys. Rev., **154** (1967), 558.
 - (40) S. G. Fishman, D. Gupta and D. S. Lieberman: Phys. Rev., **B2** (1970), 1451.
 - (41) H. Bakker, N. A. Stolwijk, L. Van der Meij and T. J. Zuurendonk: Nucl. Metall., **20** (1976), 96.
 - (42) D. Gupta, D. Lazarus and D. S. Lieberman: Phys. Rev., **153** (1967), 863.
 - (43) H. B. Huntington, N. C. Miller and V. Nerses: Acta Metall., **9** (1961), 749.
 - (44) D. Gupta and D. S. Lieberman: Phys. Rev., **B4** (1971), 1070.
 - (45) R. Hilgedieck and Chr. Herzig: Z. Metallkde., **74** (1983), 38.
 - (46) R. N. Jeffrey and D. Gupta: Phys. Rev. B, Solid State, **6** (1972), 4432.
 - (47) A. T. Donaldson and R. D. Rawlings: Acta Metall., **24** (1976), 285.
 - (48) H. Hahn, G. Froberg and H. Wever: Phys. Status Solidi, (a) **79** (1983), 559.
 - (49) G. F. Hancock and B. R. McDonell: Phys. Status Solidi, (a) **4** (1971), 143.
 - (50) G. F. Hancock and B. R. McDonell: Phys. Status Solidi, (a) **7** (1971), 535.
 - (51) L. N. Larikov, V. V. Geichenko and V. M. Falchenko: *Diffusion Processes in Ordered Alloys*, Naukova Dumka Publ., Kiev (1975); Nat. Bur. Stand., New Delhi: Amerind. Publ. Co. (1981).
 - (52) H. A. Domian and H. I. Aaronson: Trans. Met. Soc. AIME, **230** (1964), 44.
 - (53) H. A. Domian and H. I. Aaronson: *Diffusion in Body Centered Cubic Metals*, Amer. Soc. Metals, Metals Park, Ohio (1965), p. 209.
 - (54) W. C. Hagel and J. H. Westbrook: Trans. Met. Soc. AIME, **221** (1961), 749.
 - (55) M. B. Bronfin, G. S. Bulatov and I. A. Drugova: Fiz. Met. metalloved., **40** (1975), 363.
 - (56) K. Hoshino, S. J. Rothman and R. S. Averback: Symp. Diffusion Processes in High Technology Materials, Cincinnati, Ohio (1987).
 - (57) K. Hoshino, S. J. Rothman and R. S. Averback: Acta Metall., **36** (1988), 1271.
 - (58) H. Nakajima, Y. Nakamura, M. Koiwa, T. Tagasuki and O. Izumi: Scripta Met., **22** (1988), 507.
 - (59) H. Nakajima: private communication; *Collected Abstracts of the Japan Institute of Metals*, April 1995 (Tokyo), p. 343.
 - (60) D. Ansel, J. Barre, C. Meziere and J. Debuigne: J. Less Common Metals, **65** (1979), P1.
 - (61) S. Benci, G. Gasparini, F. Germagnoli and G. Schianchi: J. Phys. Chem. Solids, **26** (1965), 2059.
 - (62) S. Benci, G. Gasparini, F. Germagnoli and G. Schianchi: J. Phys. Chem. Solids, **26** (1965), 687.
 - (63) Th. Heumann and T. Rottwinkel: J. Nuclear Mater., **69-70** (1978), 567.
 - (64) E. A. Kümmerle, C. Badura, B. Sepiol, H. Mehrer and H.-E. Schaefer: Phys. Rev., **B 52** (1995), R6947.
 - (65) P. Schmidt: PhD thesis, TU Berlin, 1995.
 - (66) R. Ebeling and H. Wever: Z. Metallkde., **59** (1968), 222.
 - (67) N. Prinz and H. Wever: Phys. Status Solidi, (a) **61** (1980), 505.
 - (68) Th. Heumann, H. Meiners and H. Stür: Z. Naturforsch., **25a** (1970), 1883.
 - (69) Th. Heumann and H. Stür: Phys. Status Solidi, **15** (1966), 95.
 - (70) M. Denking and H. Mehrer: to be published.
 - (71) R. Günzel, P. Paufler and G. E. R. Schulze: *Diffusion in Metalischen Werkstoffen*. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, (1970).
 - (72) A. Y. Shinjaev: *Diffuzionnye Processij v Splavakh*, Nauka, Moskwa, (1975).
 - (73) S. Kroll, H. Mehrer, N. A. Stolwijk, Chr. Herzig, G. Frommeyer and M. Rosenkranz: Z. Metallkde., **83** (1992), 591.
 - (74) J. Rüsing and Chr. Herzig: Scripta Metall. et Mater., **33** (1995), 561.
 - (75) M. Kogachi: Defect and Diffusion Forum, **121-122** (1995), 15.
 - (76) L. Boltzmann: Wiedemanns Ann. Physik, **53** (1894), 959.
 - (77) C. Matano: Jap. J. Phys., **8** (1933), 109.
 - (78) F. Sauer and V. Freise: Z. Elektrochem., **66** (1962), 353.
 - (79) F. J. A. den Broeder: Scripta Metall., **3** (1969), 321.
 - (80) F. J. J. van Loo: Prog. Solid St. Chem., **20** (1990), 47.
 - (81) H. Schmalzried: *Solid State Reactions*, Academic Press, New York, (1974).
 - (82) J. Philibert: *Diffusion in Metals and Alloys DIMETA-88*, ed. by F. J. Kedves and D. L. Beke, Defect and Diffusion Forum **66-69** (1989), p. 995.
 - (83) J. Philibert: Defect and Diffusion Forum, **95-98** (1993), 493.
 - (84) U. Gösele: *Alloying*, ed. by J. Walters, ASM International, (1988), p. 489.
 - (85) L. S. Darken: Trans. AIME, **175** (1948), 184.
 - (86) J. R. Manning: Phys. Rev., **124** (1961), 470.
 - (87) J. R. Manning: Acta Metall., **15** (1967), 817.
 - (88) J. R. Manning: *Diffusion Kinetics for Atoms in Crystals*, van Norstrand, Princeton (1968).
 - (89) Th. Hehenkamp: Defect and Diffusion Forum, **95-98** (1993), 171.
 - (90) P. D. Desai: J. Phys. Chem. Ref. Data, **16** (1987), 109.
 - (91) T. Shimozaaki, Y. Goda, Y. Wakamatsu and M. Onishi: Defect and Diffusion Forum, **95-98** (1993), 629.
 - (92) D. L. Beke and I. A. Szabo: Defect and Diffusion Forum, **95-98** (1993), 537.
 - (93) D. L. Beke and I. A. Szabo: Proceedings of a workshop on 'Diffusion and Stresses' held in Balatonfüred (Hungary), 1995, in press.
 - (94) J. P. Pemsler and E. J. Rapoport: Met Trans., **2** (1971), 79.
 - (95) G. V. Kidson: J. Nucl. Mater., **3** (1961), 21.
 - (96) N. A. Stolwijk, H. Bracht, H.-G. Hettwer, W. Lerch, H. Mehrer,

- A. Rucki and W. Jäger: *Materials Science Forum*, **155–156** (1994), 475.
- (97) U. Schoo and H. Mehrer: to be published.
- (98) W. Sprengel, M. Denkinger and H. Mehrer: *Intermetallics*, **2** (1994), 127.
- (99) W. Sprengel, M. Denkinger and H. Mehrer: *Intermetallics*, **2** (1994), 137.
- (100) H. Mehrer, W. Sprengel and M. Denkinger: *Diffusion in Ordered Alloys*, ed. by B. Fultz, R. W. Cahn, D. Gupta, TMS, EMPMD Monograph Series, (1993), p. 51.
- (101) J. P. Neumann, Y. A. Chang and C. M. Lee: *Acta. Metall.*, **24** (1976), 593.
- (102) S. Chabik and B. Rozenfeld: *Apl. Phys.*, **25** (1981), 143.
- (103) Y. Shirai: *Bulletin Japan Inst. Metals*, **27** (1988), 869.
- (104) P. J. Schultz and I. K. McKenzie: *Positron Annihilation*, ed. by P. G. Coleman, S. C. Sharma, L. M. Diana, North-Holland Publ., (1982), p. 553.
- (105) R. J. Wasilewski: *J. Phys. Chem. Solids*, **29** (1968), 39.
- (106) G. Froberg: *Z. Metallkde.*, **72** (1981), 596.
- (107) E. W. Elcock, C. W. McCombie: *Phys. Rev.*, **109** (1958), 605.
- (108) P. Wynblatt: *Acta Metall.*, **15** (1967), 1453.
- (109) V. Arnhold: PhD Thesis, University of Münster (1981).
- (110) M. Arita, M. Koiwa and S. Ishioka: *Trans. JIM*, **29** (1988), 439.
- (111) M. Arita, M. Koiwa and S. Ishioka: *Acta Metall.*, **37** (1989), 1363.
- (112) M. Arita, M. Koiwa and S. Ishioka: *Phil. Mag.*, **60** (1989), 563.
- (113) J. Mayer, C. Elsässer and M. Fähnle: *Phys. Status Solidi*, (b) **191** (1995), 283.
- (114) W. Kohn and L. J. Sham: *Phys. Rev.*, **B 32** (1965), A1133.
- (115) R. Würschum, C. Grupp and H.-E. Schaefer: *Phys. Rev. Letters*, **75** (1995), 97.
- (116) H. Bakker, N. A. Stolwijk and M. A. Hoetjens-Eijkel: *Phil. Mag.*, **A 43** (1981), 251.
- (117) D. Berner, G. Geibel, V. Gerold and E. Wachtel: *J. Phys. Chem. Solids*, **36** (1976), 221.
- (118) A. H. Van Ommen, A. A. H. J. Waegemakers, A. C. Moleman, H. Schlatter and H. Bakker: *Acta Metall.*, **29** (1981), 123.
- (119) A. H. Van Ommen: *Phys. Status Solidi*, (a) **72** (1982), 273.
- (120) G. Vogl: *Mößbauer Spectroscopy Applied to Magnetism and Materials Science*, Vol. 2, ed. by G. J. Long and F. Grandjean, Plenum Press, New York, (1996), in print.
- (121) G. Vogl and B. Sepiol: *Acta Metall. Mater.*, **42** (1994), 3175.
- (122) R. Feldwisch, B. Sepiol and G. Vogl: *Acta Metall. Mater.*, **43** (1995), 2033.
- (123) H. Mehrer: Habilitation thesis, University of Stuttgart, 1973.
- (124) K. A. Badura, U. Brossmann, R. Würschum and H.-E. Schaefer: *Materials Science Forum*, **175–178** (1995), 295.
- (125) H.-E. Schaefer, R. Würschum and J. Bub: *Materials Science Forum*, **105–110** (1992), 439.
- (126) H. Bakker: *Phys. Status Solidi*, **28** (1968), 345.
- (127) K. Maier, H. Mehrer, E. Lessmann and W. Schüle: *Phys. Status Solidi*, (b) **78** (1976), 699.
- (128) Y. Shi: PhD Thesis, TU Berlin (1991).
- (129) Y. Shi, H. Wever and M. Mückeley: *Verhandl. DPG*, **25** (1990), 1022.
- (130) S. M. Folies and M. S. Daw: *J. Mater. Res.*, **2** (1987), 5.
- (131) Z.-Y. Xie and D. Farkas: *J. Mater. Res.*, **9** (1994), 875.
- (132) B. Sepiol and G. Vogl: *Phys. Rev. Lett.*, **71** (1993), 731.
- (133) B. Sepiol and G. Vogl: *Hyperfine Interactions*, **59** (1995), 149.
- (134) K. Hirano and Y. Iijima: *Diffusion in Solids—Recent developments*, The Metallurgical Society AIME, New York, (1984), p. 141.
- (135) Chr. Herzig, R. Willecke and K. Vieregge: *Phil. Mag.*, **63** (1991), 949.
- (136) A. M. Brown and M. F. Ashby: *Acta Metall.*, **28** (1980), 1085.
- (137) U. Brossmann, R. Würschum, K. Badura and H.-E. Schaefer: *Phys. Rev.*, **B 49** (1994), 6457.
- (138) A. Seeger and H. Mehrer: *Vacancies and Interstitials in Metals*, ed. by A. Seeger, D. Schumacher, J. Diehl and W. Schilling, North-Holland, Amsterdam, (1970), p. 1.
- (139) W. Sprengel, N. Oikawa and H. Nakajima: *Intermetallics*, (1995), in press.
- (140) J. E. Dickey: *Acta Metall.*, **7** (1959), 350.
- (141) G. Leitner: PhD thesis, Technische Universität, Dresden, (1971).
- (142) G. E. R. Schulze: *Metallphysik*, Springer Verlag, Berlin, (1974).
- (143) W. Bussmann, Chr. Herzig, W. Rempp, K. Maier and H. Mehrer: *Phys. Status Solidi*, (a) **56** (1979), 87.
- (144) S. Saito and P. A. Beck: *Trans. Met. Soc. AIME*, **218** (1960), 670.