THE FORTY-FOURTH HONDA MEMORIAL LECTURE

Diffusion in Materials—History and Recent Developments[†]

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Diffusion is a process that is fundamental in the art and science of materials. The knowledge of diffusion behaviour, therefore, is essential for the production of materials or for their use in practical applications. In the first part of this paper, a brief review is given on the historical developments of the quantitative study of diffusion: the establishment of the diffusion law by A. Fick, the first quantitative measurement of solid-state diffusion (Au in Pb) by W. C. Roberts-Austen and the demonstration of the self-diffusion in Pb using a natural radioactive isotope by G. Hevesy. In the second part, the development and the present status of our understanding of several problems: correlation effects in diffusion, fast diffusion in metals and the mechanism of diffusion in intermetallic compounds will be reviewed.

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I. Introduction

One intuitively accepts that atoms or molecules move more or less freely in gases and in liquids, but not in solids. The belief of ancient chemists, *corpora non agunt nisi soluta* (bodies do not move unless they are in solution) had long governed the way of thinking of scientists about the motion of atoms in rigid solids. Although the knowledge of carburization of iron might have suggested that diffusion occurs in the solid-state, the penetration of iron by gaseous CO was plausible. The experiment by Roberts-Austen in 1889 clearly discarded such a possibility⁽¹⁾. He showed that pure iron may be carburized by diamond *in vacuo*, at a temperature far below the melting point of iron under conditions which absolutely preclude the presence or influence of occluded gas. According to Barr⁽²⁾, the first observation of solid-state diffusion in record is that of Boyle, who is known by the equation of state of gases. In his essay⁽³⁾ of 'Porousness of Solid Bodies,' Boyle wrote:

For there is a way, by which, without the help of salts, sulphur or arsenic, one may make a solid and heavy body soak into the pores of that metal and give it a durable colour. I shall not mention the way, because of the bad use, that may be made of it. But having had the curiosity more than once to try it upon a new copper farthing, the event was, that one part of it, which I purposely forbore to tinge, remained common copper still: but the other part acquired a yellow, that differed very little, if at all, from a golden colour, the former stamp, that was impressed upon the coin, continuing visible.

This appears to be one of the earliest observation of solid-state diffusion, but somehow had been wholly for-

gotten; Barr has rightly called attention to this work in his lecture, 'The origin of quantitative diffusion measurements in solids: A centenary review⁽²⁾', given at DIMAT-96.

In the present article, first several earlier investigations that form the basis of our present understanding of diffusion processes will be reviewed. Then, brief reviews are given on the development of our understanding on (1) correlation effects in diffusion, (2) fast diffusion in metals, and (3) mechanisms of diffusion in intermetallic compounds.

II. Historical Developments of Diffusion Study

1. Fick: the establishment of the basic law of diffusion

The quantitative study of diffusion in matter started in 1855, when Adolf Fick (**Fig. 1**) proposed the renowned Fick's law and proved it for the diffusion of salt in water⁽⁴⁾. In the beginning of his paper, Fick states:

A few years ago Graham published an extensive investigation on the diffusion of salts in water, in which he more especially compared the diffusibility of different salts. It appears to me a matter of regret, however, that in such an exceedingly valuable and extensive investigation, the development of a fundamental law, for the operation of diffusion in a single element of space, was neglected, and I have therefore endeavoured to supply the omission.

It was quite natural to suppose, that this law for the diffusion of a salt in its solvent must be identical with that, according to which the diffusion of heat in a conducting body takes place; upon this law Fourier founded his celebrated theory of heat, and it is the same which Ohm applied with such extraordinary success, to the diffusion of electricity in a conductor.

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Fig. 1 Adolph Fick (1829–1901).

He measured a steady-state concentration profile of salt along a cylindrical vessel, the lower end of which was cemented, filled with solution. At the lower end the water is always maintained in a state of perfect saturation by immediate contact with solid salt; the whole being then sunk in a relatively infinitely large reservoir of pure water, the section at the upper end, which passes into pure water, always maintains a concentration = 0. After the attainment of the steady state, the linear variation of concentration was observed to prove the 'Fick's law.'

In his paper entitled: "The Origin and Present Status of Fick's Diffusion Law", Tyrrell⁽⁵⁾ made the following interesting remark on the contributions by Graham and Fick:

More than a century of experience has shown that the value of Fick's contribution to the study of diffusion in liquids, and also in its later application to gases, lies pre-eminently in the stimulus it gave, and is still giving, to accurate experimental work, and in the provision of a concise and easily appreciated form for the expression of experimental data. A glance at Graham's extensive, and almost unreadable, descriptions of quantitative studies on diffusion, will show how great a contribution this was.

Nevertheless, Graham's contribution⁽⁶⁾ to the establishment of science of diffusion should not be underestimated; first by his own achievement in the gaseous diffusion, which was discussed in some detail by Mason⁽⁷⁾ on the occasion of commemorating his centenary, secondly by motivating Fick to develop the fundamental law of diffusion, and thirdly by employing William Roberts-Austen as his personal assistant at the Mint; the next section describes the work of Roberts-Austen.

Fick's renowned paper⁽⁴⁾ is signed as 'Demonstrator of Anatomy, Zürich.' He entered the University of Marburg with the intention to specialize in mathematics, but switched to medicine on the advice of an elder brother. Adolph Fick became an outstanding figure in

the nineteenth century physiologists who applied the concepts and methods of physics to the study of living organisms, and thereby laid the foundations of modern physiology.

2. Roberts-Austen: the first quantitative measurement of solid-state diffusion

William Roberts-Austen (Fig. 2) graduated from the Royal School of Mines in 1865 when he became assistant to Thomas Graham at the Mint, where he studied salt diffusion and the absorption of hydrogen by metals and became a skilled assayer capable of measuring the most minute quantities of gold. His long connection with Graham's researches led him to extend the work of Graham on liquid diffusion to metals. In diffusion experiments, it is essential to keep the temperature constant for a long period of time and to measure it accurately. The difficulty in measuring temperature was overcome by adopting Le Chatelier's platinum based thermocouples and devising an 'autographically recording pyrometer.' In his paper of 1896 entitled 'Diffusion of Solid Metals. Gold, Diffusing into Solid Lead'⁽⁸⁾, he states:

The following experiments constitute, so far as I am aware, the first attempt to actually measure the diffusivity of one solid metal in another.

The experiments were made by using cylindrical rods of lead, 14 mm in diameter and 4.5 to 70 mm in length, at the end of which thin plates of gold had been fused. Diffusion anneals were made at temperatures between 100° and 250°C (75°C below the melting temperature). It is surprising to observe that the values of the diffusion coefficients of Au in Pb reported by him are similar to those determined by modern techniques in the 1960's and 1970's using radio-active isotopes. The choice of the system Pb–Au was really fortunate to demonstrate the otherwise generally slow diffusion processes in solids; the diffusion of noble metals in Pb is now known to be exception-

Fig. 2 William Chandler Roberts-Austen (1843–1902).

ally fast, the detailed mechanism of which is still subject in dispute. In a later section, some additional remarks are made on fast diffusion.

It is of interest to quote the following statement of Barr⁽³⁾:

In these papers Roberts-Austen set the style for diffusion measurements in solids, even his convention of quoting diffusion coefficients in units of $\text{cm}^2 \text{ day}^{-1}$ persisted for forty years and today his papers are as easily read and understood as any modern one.

The most surprising omission in his diffusion paper is any discussion or analysis of the temperature dependence of the diffusion coefficient although the metallurgist R. F. Mehl⁽⁹⁾ attributes to Roberts-Austen relating that temperature dependence to the concept of activation energy introduced by Arrhenius⁽¹⁰⁾ in 1889. It is possible that this linkage is made in the Reports of the Alloys Research Committee chaired by Roberts-Austen between 1891 and 1899. These reports are not readily accessible and the question is still not settled. Certainly, by 1922 the connection had been made by Dushman and Langmuir⁽¹¹⁾.

Earlier Tammann and Schönert⁽¹²⁾ used for the temperature dependence the empirical relation: $D = \exp(-a + bT)$; for a limited temperature range this relation gives a reasonable fit to experimental data.

3. Hevesy: the first measurement of self-diffusion using radioactive isotopes

The idea of self-diffusion was introduced by Maxwell, when he discussed the rate of diffusion of gases. No further use was made of this concept until fifty years later, when Hevesy (Fig. 3) made the experiment on self-diffusion in liquid (1920) and solid lead (1921) by using natural radioactive isotopes, ^{210}Pb and ^{212}Pb ⁽¹³⁾⁽¹⁴⁾.

The diffusion couple was prepared in the following way. The inactive lead was melted in one limb of the Y-shaped hard glass tube (about 3 mm in diameter) and, after it had solidified, the fused active lead contained in the

other limb was poured on, thereby producing a cohesive metallic cylinder. After holding the couple at 280°C for 400 days, the diffusion was hardly detectable; the diffusion coefficient was concluded to be less than 0.0001 cm^2 per day. Further experiments were made by using thin films and with ^{212}Pb as the tracer to derive quantitative results⁽¹⁵⁾⁽¹⁶⁾.

Hevesy was born in Hungary and educated in Budapest, Berlin and later in Freiburg, where he took degree in 1908. He proceeded to Zürich to carry out research in the field of high temperature chemistry. In the course of the research he felt the necessity of acquiring experience in the field of the conductivity of electricity in gases. Thus, he left for Manchester to work under Rutherford. During his stay in Manchester from 1911 to 1914, Hevesy witnessed some of the greatest discoveries in the history of physics. At that time, Rutherford was much interested to come into the possession of a strong radium D sample. Large amounts of radium D were stored in the laboratory, but imbedded in huge amounts of lead. The following is an excerpt from his autobiography⁽¹⁷⁾:

One day I met Rutherford in the basement of the laboratory where the lead chloride was stored. He addressed me by saying: 'If you are worth your salt, you separate radium D from all that nuisance of lead.' Being a young man, I was an optimist and felt sure that I should succeed in my task. Trying during a year all sorts of separation methods and making the greatest efforts, it looked sometimes as if I succeeded, but I soon found out that it was radium E, the disintegration product of radium D, a bismuth isotope, which I separated. The result of my efforts was entire failure. To make the best of this depressing situation, I thought to avail myself of the fact that radium D is inseparable from lead, and to label small amounts of lead by addition of radium D of known activity obtained from tubes in which radium emanation decayed. From such tubes pure radium D can be obtained.

He received the Nobel prize in 1943 for his work on the use of isotopes as tracers in the study of chemical processes. His name is also remembered for the discovery of the 72nd element in the periodic table, hafnium (Hf).

III. Vacancy Mechanism and Correlation Effect in Diffusion

With the accumulation of the values of diffusion coefficients in various metals and alloys, the mechanism of diffusion attracted much interest of scientists. Various mechanisms such as interstitial-, direct and indirect exchange- and vacancy mechanisms, were proposed. The calculation of activation energies for these processes suggested the vacancy mechanism as the most plausible⁽¹⁸⁾. The observation of the Kirkendall effect^{(19),(20)} was taken as strong evidence in favour of such mechanisms resulting in net mass transfer; the interdiffusion experiments on a diffusion couple of Cu and Cu-Zn revealed the motion of markers placed at the interface, which can be explained only by the different rates of diffusion of Cu and Zn atoms.

Fig. 3 George Hevesy (1885–1966).

Studies of basic properties of lattice defects revealed that the sum of the formation energy and the activation energy for migration of a vacancy is very close to the activation energy for self-diffusion in the relevant metal. This was taken as strong evidence supporting the vacancy mechanism.

In pure metals, vacancies can be regarded as ideal random walkers. Nevertheless, the motion of a tracer atom resulting from the site exchange with vacancies is not ideally random; the tracer atom just completed the site exchange with a vacancy has a more than random probability of jumping back to the original site in its next jump. This correlation of successive jumps of atoms in the vacancy mechanism was first pointed out by Bardeen and Herring⁽²¹⁾. Compaan and Haven⁽²²⁾ calculated the correlation factor for various lattices. The calculation of the correlation factors for various processes has become one of the main problems in diffusion kinetics. Detailed accounts for the correlation effect and the method of calculations have been given by Manning⁽²³⁾ and by LeClaire⁽²⁴⁾. Various methods of calculation by the Monte Carlo method were reviewed by Murch⁽²⁵⁾.

The present authors have applied the random walk theory by Montroll and Weiss⁽²⁶⁾ for the calculation of the correlation factors in the diffusion on various three dimensional lattices⁽²⁷⁾⁽²⁸⁾. The significance of the approximate formula of the correlation factor, f , and the coordination number, z , $f = 1 - 2/z$, has also been discussed⁽²⁹⁾. For self-diffusion in pure metals, the correlation factor is a constant between 0.5 and 1, whereas that for impurity diffusion is a complex function of jump frequencies of vacancy. In the case of f.c.c. metals, at least five jump frequencies of vacancy should be defined to describe the motion of both solute (or impurity) and solvent atoms. Such calculations of the correlation factors for impurity diffusion have been performed by LeClaire and Lidiard⁽³⁰⁾, and by Manning⁽³¹⁾. Later the present authors have made a calculation of the quantity by using Green's function⁽³²⁾, since no approximation is involved in the calculation, the result is rigorous in the framework of the five jump-frequency model.

IV. Fast Diffusion

As stated above, it is now generally accepted that the self-diffusion occurs via the vacancy mechanism. Impurity atoms substituting solvent atoms are also expected to diffuse with the same mechanism. In that case, the impurity diffusion coefficient should not be much different from that of the self-diffusion. **Figure 4** shows the relative magnitudes of impurity diffusion coefficient, D_i/D_s , in several host metals, Cu, Fe, Pb and α -Ti. For metallic solutes in Cu, the impurity diffusion coefficients are in the range between 1/30 (Nb) and 20 (Sb). As iron as the host, the substitutional solutes diffuse at the rates between 1/10 and 10 of the self-diffusion coefficients; the interstitial solutes such as carbon and nitrogen diffuse very fast. As stated in Section II 2, Au in Pb is the first system for which the quantitative measurement of solid-state

Fig. 4 The ratio of impurity-diffusivity D_i to self-diffusivity D_s in several metals⁽⁴⁴⁾. For Cu, Fe and Pb, the values at $0.8T_m$ (the melting temperature) are shown. The bars indicate the range of values for various metallic solutes. For Fe, the hypothetical melting temperature of γ -iron has been proposed to be 1809 K (A. J. Ardell: Acta Metall., **11** (1963), 591). Thus, $0.8T_m = 1447$ K. The hypothetical melting temperature of α -Ti is 1782 K. In reality α -Ti does not exist at $0.8T_m$ ($=1382$ K); the temperature of 1073 K was chosen arbitrarily.

diffusion has been reported; the ratio, D_i/D_s , amounts to 10^5 . The anomalously large diffusivity has been confirmed by the radio-active tracer technique later. Furthermore, similar trends were found for the other noble elements, Cu and Ag.

Such phenomena that metallic solutes diffuse at a rate several orders of magnitudes higher than that of the self-diffusion are referred to as fast diffusion. An extensive review of the phenomenon has been given by Warburton and Turnbull in 1975⁽³³⁾; fast diffusion has been observed in a variety of hosts: polyvalent metals (Pb, Sn, Tl and In), alkaline metals (Li, Na and K), lanthanide and actinide metals (Pr, La and U) and semiconductors (Ge and Si).

As the mechanism of fast diffusion, several models have been proposed.

(a) Frank and Turnbull⁽³⁴⁾ proposed a dissociative mechanism for Cu diffusion in Ge by supposing that the Cu is distributed among both interstitial and substitutional sites and those at interstitial sites diffuse very fast.

(b) Split interstitial of host-impurity, which was designated as diplon by Warburton and Turnbull⁽³³⁾, was suggested as a defect effecting transport.

(c) Interstitial-vacancy pairs were discussed by Miller⁽³⁵⁾ and by Warburton⁽³⁶⁾.

All these models commonly assume essentially the presence of some kind of interstitial solutes. Various attempts to obtain direct evidence of the interstitial solute atoms have been unsuccessful⁽³³⁾.

It has been suggested that measurements of the isotope

effect may yield useful information in identifying the mechanism of diffusion. The isotope effect coefficient defined by

$$E = \frac{\partial \ln D}{\partial \ln m^{-1/2}}, \quad (1)$$

where m is the mass of the diffuser, is known to be close to unity for the conventional interstitial diffusion such as C in Fe⁽²³⁾. The value of E for fast diffusion such as Au, Ag and Cu in Pb has been reported to be about 0.25; the smaller value of E has been considered to be inconsistent with the interstitial mechanism. The present authors have examined the many-body effect in the elementary process in diffusion, and suggested that the small E does not necessarily exclude the interstitial-type mechanism⁽³⁷⁾.

In Fig. 4, the data for diffusion in α -Ti matrix are also given. Since the diffusion in hexagonal crystals is anisotropic, the diffusion experiment should be made using single crystal specimens for quantitative study. The present authors have made such measurements for a series of transition elements: Co⁽³⁸⁾, Fe⁽³⁹⁾, Ni⁽⁴⁰⁾, Mn⁽⁴¹⁾ and Cr⁽⁴²⁾, and also for P⁽⁴³⁾. **Figure 5** shows these data together with the self-diffusion data measured on polycrystalline specimens. Transition metal elements and P diffuse at rates 10^3 to 10^5 times faster than that of the self-diffusion; a review on the diffusion in α -Ti was given in Ref. 44.

The data for Co, Fe and Ni is exhibited in Fig. 4. Note that the similar trends have been observed for diffusion in α -Zr, which has been studied extensively by Hood and his coworkers⁽⁴⁵⁾. **Figure 6** shows the diffusion coefficients of various solutes at 1100 K in α -Ti and in α -Zr plotted

Fig. 5 Temperature dependence of self- and impurity diffusion coefficients in α -Ti⁽⁴⁴⁾.

Fig. 6 Diffusivity (1100 K) versus metallic radius in α -Ti and α -Zr.

against atomic radius; smaller atoms diffuse faster. Such size effect also supports that the operative mechanism of diffusion is of the interstitial type. The self-diffusion in α -Zr is known to be affected strongly by the presence of very small amount, several 10 ppm, of Fe⁽⁴⁶⁾, which is of great interest in relation to the mechanism of the fast diffusion of Fe atoms. An attempt of obtaining microscopic information on the atomistic processes of iron diffusion in α -Zr has been made by in-beam Mössbauer spectroscopy; some motion of Fe was observed but not those resulting in long-range migration⁽⁴⁷⁾.

V. Diffusion Mechanisms in Intermetallic Compounds

In pure metals or solid solutions, self-diffusion occurs by random motion of vacancies. In ordered alloys or compounds, however, random vacancy motion is not possible as it would disrupt the equilibrium ordered arrangement of atoms on lattice sites. Thus, the mechanism of diffusion in this type of materials is of great interest. As a plausible mechanism, Huntington⁽⁴⁸⁾ was the first to suggest the possibility of a six-jump vacancy cycle that allows diffusion to take place exclusively by means of the nearest neighbour vacancy jumps. Therefore, first this mechanism will be discussed. Then we will discuss possible mechanisms proposed for the B2 and the L1₂ structures.

1. The six-lump vacancy cycle (SJVC) mechanism

This mechanism is explained for the case of the two-dimensional square lattice of an ordered A-B alloy as shown in **Fig. 7**; A atoms occupy α sublattice sites and B atoms β sub-lattice sites. If the vacancy on the α sublattice makes a series of six jumps indicated by the arrows, the number of wrong bonds increases as follows:

Fig. 7 Six jump vacancy cycle in the ordered A-B alloy on the square lattice. A and B atoms sit on α - and β -sublattice sites, respectively. After six jumps of the A atom vacancy (α vacancy) in the directions indicated by the arrows, the vacancy changes the site with the A atom involved in the cycle, and the two B atoms exchange the sites each other.

Fig. 8 Schematic of energy changes during six-jump vacancy cycle. Six individual vacancy jump frequencies are required to define the cycle, as written under the figure.

$$0 \rightarrow 3 \rightarrow 5 \rightarrow 6 \rightarrow 5 \rightarrow 3 \rightarrow 0.$$

Namely, the number increases in the first three jumps but decreases in the last three jumps, recovering the fully ordered arrangement in the final configuration. The energy change during the process may be illustrated as shown in Fig. 8.

In order to derive the expression for the diffusion coefficient for this process, one has to first obtain the expression for the average frequency of the vacancy initially at configuration 1 to attain configuration 7. This can be calculated by applying the concept of the mean first passage time known in the theory of stochastic processes⁽⁴⁹⁾. The average frequency $\bar{\nu}$ is given by the reciprocal of the mean first passage time, $\bar{t}$, for the vacancy to attain the final configuration. Once $\bar{\nu}$ is obtained, one need not worry about the details of the cycle; the diffusion may be

regarded as that by a simple vacancy mechanism on a new square lattice with a lattice constant of $\sqrt{2}a$. By considering that β vacancies also contribute (and vice versa) to the diffusion of A atoms, the diffusion coefficients for A and B atoms, D_A and D_B can be written as

$$D_A = \frac{1}{2} \bar{\nu}^\alpha C_{V_\alpha} a^2 f_A + \bar{\nu}^\beta C_{V_\beta} a^2 f_B, \quad (2a)$$

$$D_B = \frac{1}{2} \bar{\nu}^\beta C_{V_\beta} a^2 f_A + \bar{\nu}^\alpha C_{V_\alpha} a^2 f_B, \quad (2b)$$

where C_{V_α} and C_{V_β} are the vacancy concentrations, f_A and f_B are correlation factors of respective sublattices. The details were given in Ref. 50. The SJVC mechanism is not restricted to the square lattice; the mechanism has been discussed for the B2 and $L1_2$ structures, as described below.

2. Diffusion mechanisms in B2 compounds

The diffusion behaviour in the B2 compounds has been more extensively studied than that in compounds of any other crystal structures, both experimentally and theoretically, as reviewed previously⁽⁵¹⁾. Possible mechanisms are discussed briefly below.

(1) The SJVC mechanism

The SJVC mechanism for the B2 structure was first discussed by Wynblatt⁽⁵²⁾. Consider the case in which there is a vacancy in the α sublattice in an otherwise perfect B2 crystal as depicted in Fig. 9. The cycle in Fig. 9(a) causes a net transport of the vacancy across a $[110]$ face-diagonal and will be referred to as a 110-type cycle, whereas the cycles in Figs. 9(b) and 9(c) cause a net transport of the vacancy across a $[100]$ cube edge and will be referred to as bent 100- and straight 100-type cycles, respectively, depending upon whether all six jumps are confined to a single plane or not. The number of wrong bonds are examined as in the case of the square lattice; the potential energy change during the cycle can also be schematically expressed by Fig. 8. The complication in

Fig. 9 Six-jump vacancy cycle in the B2 lattice⁽⁵²⁾. The arrows indicate the path of the vacancy (the lower figures show the atom arrangement after the complete cycle): (a) 110-jump cycle; (b) bent 100-jump cycle; (c) straight 100-jump cycle.

comparison to the case of the square lattice is the presence of the three types of cycles. However, this can be dealt with rigorously and one can eventually derive expressions for the diffusion coefficients, which are essentially similar to those given in eq. (2); for details see Ref. 53.

An important result of the SJVC mechanism is the strong coupling between the two diffusion coefficients, D_A and D_B ; this is evident by observing that the process illustrated in Fig. 7 results in the displacements of one A and two B atoms. If one neglects the correlation factors, the limit of the ratio, D_B/D_A , is given by

$$\frac{1}{2} < D_B/D_A < 2. \quad (3)$$

A rigorous calculation that includes correlation effects⁽⁵³⁾ yields

$$(2.034)^{-1} < D_B/D_A < 2.034. \quad (4)$$

The ratios of many of the measured component diffusion coefficients in the B2 structure do fall within the limits of eq. (4), and this has been considered as ‘proof’ of the operation of the SJVC mechanism for such compounds.

If monovacancies are only the defects existing in an otherwise perfectly ordered B2 alloy, the SJVC process is considered to be the most probable path; the other types of vacancy movements would bring about configurations of much higher energy. If the energy increase in creating wrong bonds is small, vacancies tend to move more randomly; in such a case the diffusion should be more properly treated on the basis of different models. In this respect, it is interesting to examine the diffusion behav-

Fig. 10 Energy-displacement curves for vacancy jumps in NiAl (Mishin and Farkas⁽⁵⁶⁾). (a) The 110-type six-jump vacancy cycle. (b) The next nearest neighbour jump.

our of various alloys in comparison to the respective ordering energy (eV units) as listed below⁽⁵⁴⁾.

CuZn	AgMg	AuCd	AuZn	FeAl	CoGa	NiGa	PdIn	NiAl
0.12	0.19	0.2	0.27	0.32–0.36	0.38–0.43	0.45–0.49	0.64	0.69–0.74

For alloys with smaller ordering energies: CuZn, AgMg, AuCd and AuZn, the ratio, D_B/D_A , falls in the range given in eq. (4), consistent with the SJVC mechanism. For NiAl with the largest ordering energy, only the diffusivity of Ni is available. Lutze-Birk and Jacobi⁽⁵⁵⁾ measured the diffusivity of In, which is known to substitute for Al. For the stoichiometric compound, the ratio, D_{Ni}/D_{In} is 6.0; the authors concluded that the next nearest neighbour jumps contribute to the diffusion to some extent.

The first calculation of energy on the SJVC mechanism was performed by Wynblatt⁽⁵²⁾ using Morse potentials for AgMg. The calculation showed that the overall migration energy was less than that for next nearest neighbour jumps. Recently Mishin and Farkas⁽⁵⁶⁾ investigated NiAl using the embedded atom potentials and showed that the SJVC mechanism is not energetically most favourable, but is highly competitive with the n.n.n. jumps, as seen in Fig. 10; the effective activation energy for Ni vacancy migration for the SJVC mechanism (the maximum energy in the cycle) is 2.442 eV, which is to be compared

with 2.074 eV for the n.n.n. jump. Calculations using an ab initio pseudo-potential method for FeAl showed that for Fe the SJVC is not competitive with n.n.n. jumps⁽⁵⁷⁾.

The isotope effect in diffusion based on the SJVC mechanism has been discussed in detail in Ref. 58. The isotope effect coefficient defined by eq. (1) can either be large or small, depending on the relative magnitudes of the individual jump frequencies of vacancy; the measurement of the isotope effect would not yield a clear clue in identifying the operative mechanism of diffusion.

(2) Anti-structure bridge (ASB) mechanism

Kao and Chang⁽⁵⁹⁾ have proposed a new mechanism, termed anti-structure bridge (ASB) mechanism, to account for the diffusion at large deviations from stoichiometry. The idea is that when there is a sufficient number of anti-structural atoms, such atoms, along with the home lattice atoms of the same species, can form a percolating substructure on which a vacancy can diffuse by nearest neighbour jumps without creating wrong bonds. They have attempted to explain the composition depen-

dence of the diffusivities in AuCd, CoGa and AuZn with a combination of the ASB and SJVC mechanisms. The deviation from stoichiometry necessary to form a continuous bridge has been estimated as about 0.016.

The validity of this mechanism has been critically examined by Belova and Murch⁽⁶⁰⁾. According to their computer simulation, the percolation threshold in the B2 structure at stoichiometry occurs when the degree of long-range order is less than 0.72 or when the composition of the percolating species is greater than 0.565 (or 0.065 in the deviation from the stoichiometry, which is to be compared with 0.016 by Kao and Chang) at very high levels of order. The analytical results are consistent with these evaluations; the estimate by Kao and Chang is too small. This composition, 0.565, is outside the composition stability of many highly ordered compounds with the B2 structure. Belova and Murch⁽⁶¹⁾ suggest that the ASB mechanism concept needs to be extended to allow for dynamically changing percolating regions rather than the static structures on which the existing calculations are based.

(3) Triple defect mechanism

For some intermetallic compounds such as CoGa, the ratio of the two diffusion coefficients is outside the range predicted for the SJVC mechanism. Stolwijk *et al.* proposed a new mechanism termed as the triple defect mechanism⁽⁶²⁾. This mechanism is basically a divacancy mechanism as illustrated in Fig. 11. In Fig. 11(b), the defect takes a triple defect configuration: $2V_\alpha + A_\beta$; this state is considered to be the most stable. In this model, A atoms are assumed to diffuse by nearest neighbour jumps, while B atoms by next nearest neighbour jumps. The ratio D_B/D_A , predicted for this mechanism⁽⁶³⁾ has the limits:

$$(13.3)^{-1} < D_B/D_A < 13.3. \quad (5)$$

Although triple defect disorder is accepted as the dominant defect in several compounds such as CoGa, NiGa, NiAl and CoAl, it is not clear if the constituents, two vacancies and one anti-structural atom, favour to be near around each other as shown in Fig. 11(b).

Fig. 11 Jump sequence during triple-defect migration in a two-dimensional analogue of the B2 structure (Stolwijk *et al.*⁽⁶²⁾). A atoms (filled circles) may occupy B atom (open circles) sites to form anti-structure atoms, while B atoms always remain on its own sublattice sites; B atoms jump into next nearest neighbour sites. The intermediate configuration (b) corresponds to triple defect, and the other two, (a) and (c), to divacancy configuration.

(4) Other mechanisms

In the above, we have discussed several specialized mechanisms. Since the vacancy motion is dictated by the local environment, complete diffusion behaviour should be described with the correct environment sampling and averaging. The calculation by Kikuchi and Sato⁽⁶⁴⁾ with the path probability method and that by Bakker⁽⁶⁵⁾ with the random alloy model are analytical approaches in this direction, and Monte Carlo calculations are evidently suitable to deal with generalized vacancy motion. The specialized mechanisms are subsets of a general vacancy motion; the SJVC mechanism is simply a small set of pathways taken by the vacancy. Therefore, one should be careful in identifying the operative mechanism of diffusion in actual materials.

3. Diffusion mechanisms in L1₂ compounds

(1) The ordered Cu₃Au rule

Figure 12 illustrates the atomic arrangement of an A₃B compound of the L1₂-type structure; the arrangement is not symmetrical for A and B atoms. A atoms occupy the face-centre sites, which constitute the α sublattice, and B atoms occupy the cube-corner sites, which constitute the β sublattice. While an A atom has eight atoms of the same species at the nearest-neighbour sites (Fig. 12(b)), a B atom is surrounded by twelve unlike atoms (Fig. 12(c)). Thus, if the diffusion occurs by vacancy jumps to nearest neighbour sites, A atoms are expected to diffuse much faster than B atoms; a jump of a B atom to the nearest-neighbour site inevitably destroys the ordered arrangement, while no disordering occurs for the jump of an A atom. The faster diffusion of the major element A in compounds of type A_mB_n where the ratio m/n is greater than

Fig. 12 Atom arrangement in an A₃B alloy of the L1₂-type structure. The unit cell, (a), and the arrangements of atoms surrounding an A- (b) and a B- (c) atoms.

2, has been recognized and termed ‘the ordered Cu_3Au rule’ by d’Heurle and Gas⁽⁶⁶⁾.

The α sublattice by itself is a cubic lattice with the coordination number eight. This lattice may be referred to as the NbO lattice; niobium and oxygen atoms in niobium monoxide arrange themselves respectively to form the α sublattice. The diffusion of the major element A in an A_3B compound of the L_{12} -type is most naturally considered to occur via the simple vacancy mechanism on such a lattice. Properties related to random walks, self- and impurity diffusion on the NbO lattice have been discussed in previous papers⁽⁶⁷⁾⁽⁶⁸⁾.

(2) Diffusion in the Ni-based L_{12} type compounds

Recently, the present authors have analysed the diffusion behaviour of the Ni-based compounds of the L_{12} type structure: Ni_3Al , Ni_3Ga and Ni_3Ge ⁽⁶⁹⁾; the temperature dependence of diffusion coefficients are given in Fig. 13. The following trends are observed.

(a) The diffusivity of the major element, Ni, is roughly equal for the three compounds. It is lower than the self-diffusivity in pure Ni by an order of magnitude.

(b) The diffusivity of the minor element is very different for the three compounds. The ratio of the diffusion coefficient of the minor element to that of the major element, D_B/D_A , at, for example, the temperature $T=0.85T_m$ is

Ni_3Al	0.2–0.4
Ni_3Ga	0.4–0.8
Ni_3Ge	0.007

When the very low diffusivity of Ge in Ni_3Ge was discovered⁽⁷⁰⁾, it appeared natural and understandable from

Fig. 13 Self-diffusion coefficients in Ni_3Al , Ni_3Ga , Ni_3Ge and pure Ni. The diffusivity is that of the element underlined in the tag.

the atomic arrangement. However, in Ni_3Ga , the diffusivity of the minor element turns out to be of the same order of magnitude as that of the major element⁽⁷¹⁾.

(3) Possible mechanisms

The observation that the diffusivities of the major element Ni are substantially the same in the three compounds, is consistent with the intuitive expectation that it diffuses on its own α sublattice by a simple vacancy mechanism. The question is how the minor element B, fully surrounded by unlike atoms, can diffuse, which has been reviewed in a previous paper⁽⁷²⁾. We shall briefly discuss several possible mechanisms below.

Six jump vacancy cycle

Hancock⁽⁷³⁾ has shown that two different cycles, bent- and straight cycle, are possible for an α -vacancy as depicted in Fig. 14; similar cycles exist also for a β -vacancy. The procedure for the derivation of the diffusion coefficient for SJVC has been described in the previous paper⁽⁷⁴⁾, and the detailed numerical data are given in Ref. 75. The ratio of the two diffusion coefficients is found to be

Fig. 14 Six-jump vacancy cycle for an α -vacancy in the L_{12} lattice⁽⁷³⁾. (a) straight cycle, (b) bent cycle.

Fig. 15 Divacancy in the L_{12} lattice. (a) Possible vacancy jumps. (b) Mid-point lattice; each lattice point corresponds to the mid-position of the two vacancies.

$$1.17 < D_B/D_A < 9.40. \quad (6)$$

Thus, if the major element A does not diffuse on its own sublattice by the simple vacancy mechanism due to some reason or other, and the SJVC is the only operative mechanism, then the minor element B diffuses faster than the major element A.

Divacancy or triple defect mechanism

Similarly to the case of the B2 structure, the diffusion of B atoms is possible by a divacancy mechanism or triple defect mechanism also for the L1₂ structure. We have calculated the correlation factors and the ratio of the diffusion coefficients for this mechanism. The two vacancies are situated at nearest neighbour positions as shown in Fig. 15(a). The divacancy is assumed not to dissociate; B atoms jump into next-nearest-neighbour positions. This means that four A atoms and two B atoms are able to jump into the divacancy at any moment. The position of the divacancy is characterized by its mid-point; Fig. 15(b) shows the mid-point lattice. The correlation factors have been calculated by analysing random walks on the mid-point lattice; details will be reported in a separate paper⁽⁷⁶⁾. The ratio of the two diffusion coefficients is found to be

$$0.204 < D_B/D_A < 16.39. \quad (7)$$

The α sublattice vacancy mechanism

When appreciable numbers of vacancies V_α and antisite atoms B_α exist, the diffusion of B atoms can be achieved by the migration of such antisite atoms over the α sublattice. The details of this model has been fully discussed in Ref. 69. With this model, the diffusion coefficient is proportional to the number of antisite atoms B_α , and to that of vacancies V_α . Thus, for quantitative analysis and discussion of diffusion behaviour, detailed knowledge on point defects are required for the relevant material. Such analysis has been made for Ni₃Al⁽⁷⁷⁾. The model accounts well for the magnitudes of the diffusion coefficients of Ni in the three compounds, and the relative magnitudes of the diffusion coefficients of Al and Ni in Ni₃Al relative to those in pure Ni. The principal features observed in the self-diffusion in Ni₃Ga and Ni₃Ge can also be understood in terms of the α sublattice vacancy mechanism.

VI. Concluding Remarks

The quantitative study of diffusion in solids began by the work of Roberts-Austen. In one hundred-odd years after his measurements of Au diffusion in Pb reported in 1896, a sound basis has been laid at least for the phenomenological theory of diffusion. For atomistic details of the diffusion, however, a number of problems still remain unsolved; to name a few, the mechanism of fast diffusion and that of diffusion in intermetallic compounds, as reviewed in this paper. In the latter case, the argument in identifying the operative mechanism has

been mostly based on the ratio of the diffusion coefficients of the two constituent atoms of the respective compounds. Evidently, further developments of experimental techniques that is able to yield the information on individual atomic jumps, such as the Mössbauer spectroscopy, are required. In parallel, theoretical efforts to predict the location or state of solute atoms in alloys or compounds, and the dynamics of atom movements are desirable for the better understanding of the diffusion processes in solids.

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REFERENCES

- (1) W. C. Robert-Austen: *Nature*, **41** (1889), 14.
- (2) L. W. Barr: *Defect Diffusion Forum*, **143-147** (1997), 3.
- (3) R. Boyle: *Experiments and Considerations about the Porosity of Bodies*, in two Essays, London, St. Paul's Churchyard, (1684), 777.
- (4) A. Fick: *Poggendorff's Annalen*, **94** (1855), 59; *Philos. Mag.*, **10** (1855), 30.
- (5) H. J. V. Tyrrell: *J. Chem. Education*, **41** (1964), 397.
- (6) See, for example, T. Graham: *Philos. Trans. Roy. Soc.*, **151** (1861), 183.
- (7) E. A. Mason: *Philos. J.*, **7** (1970), 99.
- (8) W. C. Robert-Austen: *Philos. Trans. Roy. Soc.*, **A187** (1896), 383.
- (9) R. F. Mehl and R. W. Cahn: *The Historical Development of Physical Metallurgy*, in *Physical Metallurgy*; third, revised and enlarged edition, Ed. by R.W. Cahn and P. Haasen, Elsevier Science, (1983), 1.
- (10) S. Arrhenius: *Z. Phys. Chem.*, **4** (1889), 226.
- (11) S. Dushman and I. Langmuir: *Phys. Rev.*, **20** (1922), 113.
- (12) G. Tammann and K. Schöner: *Z. Anorg. Chem.*, **122** (1922), 27.
- (13) J. Groh and G. v. Hevesy: *Ann. Phys.*, **63** (1920), 85.
- (14) J. Groh and G. v. Hevesy: *Ann. Phys.*, **65** (1921), 216.
- (15) G. v. Hevesy and A. Obrutsheva: *Nature*, **115** (1925), 674.
- (16) G. v. Hevesy, W. Seith and A. Keil: *Z. Phys.*, **79** (1932), 197.
- (17) G. Hevesy: *Adventures in Radioisotope Research, The Collected Papers of George Hevesy*, Pergamon, (1962).
- (18) H. B. Huntington and F. Seitz: *Phys. Rev.*, **61** (1942), 315.
- (19) E. O. Kirkendall: *Trans. AIME*, **147** (1942), 104.
- (20) A. D. Smigelskas and E. O. Kirkendall: *Trans. AIME*, **171** (1947), 130.
- (21) J. Bardeen and C. Herring: *Atom Movements*, Ed. by J. H. Hollomon, American Society for Metals, (1951), 87.
- (22) K. Compaan and Y. Haven: *Trans. Faraday Soc.*, **52** (1956), 786; **54** (1958), 1498.
- (23) J. R. Manning: *Diffusion Kinetics for Atoms in Crystals*, R. Van Nostrand, (1968).
- (24) A. D. LeClaire: *Physical Chemistry: An Advanced Treatise*, Ed.

- by H. Eyring, D. Henderson and W. Jost, Academic Press, Vol. 10, (1970), 261.
- (25) G. E. Murch: *Diffusion in Crystalline Solids*, Ed. by G. E. Murch and A. S. Nowick, Academic Press, (1984), 379.
- (26) E. W. Montroll and G. H. Weiss: *J. Math. Phys.*, **6** (1965), 167.
- (27) M. Koiwa and S. Ishioka: *J. Stat. Phys.*, **30** (1983), 477.
- (28) M. Koiwa and S. Ishioka: *Solute-Defect Interaction, Theory and Experiment*, Proceedings of the International Seminar, Kingston, Canada, Ed. by S. Saimoto, G. R. Purdy and G. V. Kidson, Pergamon, (1986), 232.
- (29) I. A. Szabó, M. Koiwa and S. Ishioka: *Philos. Mag. B*, **64** (1991), 83.
- (30) A. D. LeClaire and A. B. Lidiard: *Philos. Mag.*, **1** (1956), 518.
- (31) J. R. Manning: *Phys. Rev.*, **136** (1964), 1758; *Phys. Rev. B*, **6** (1972), 1344.
- (32) M. Koiwa and S. Ishioka: *Philos. Mag.*, **47** (1983), 927.
- (33) W. K. Warburton and D. Turnbull: *Diffusion in Solids; Recent Developments*, Ed. by A. S. Nowick and J. J. Burton, Academic Press, (1975), 172.
- (34) F. C. Frank and D. Turnbull: *Phys. Rev.*, **104** (1956), 617.
- (35) J. W. Miller: *Phys. Rev.*, **188** (1969), 1074.
- (36) W. K. Warburton: *Phys. Rev. B*, **7** (1973), 1341.
- (37) S. Ishioka, H. Nakajima and M. Koiwa: *Philos. Mag. A*, **55** (1987), 359.
- (38) H. Nakajima, M. Koiwa, Y. Minonishi and S. Ono: *Trans. JIM*, **24** (1983), 655.
- (39) H. Nakajima, M. Koiwa and S. Ono: *Scripta Metall.*, **17** (1983), 1431.
- (40) H. Nakajima and M. Koiwa: *Titanium, Science and Technology*, Ed. by G. Lütjering, U. Zwicker and W. Bunk, Deutsche Gesellschaft für Metallkunde e.V., (1985), 1759.
- (41) Y. Nakamura, H. Nakajima, S. Ishioka and M. Koiwa: *Acta Metall.*, **36** (1988), 2787.
- (42) H. Nakajima, K. Ogasawara, S. Yamaguchi and M. Koiwa: *Mater. Trans., JIM*, **31** (1990), 249.
- (43) H. Nakajima, J. Nakazawa, Y. Minonishi and M. Koiwa: *Philos. Mag. A*, **53** (1986), 427.
- (44) H. Nakajima and M. Koiwa: *ISIJ International*, **31** (1991), 757.
- (45) G. M. Hood: *Defect Diffusion Forum*, **95–98** (1993), 755.
- (46) M. Lubbehusen, K. Vieregge, G. M. Hood, H. Mehrer and C. Herzig: *J. Nucl. Mater.*, **182** (1991), 164.
- (47) Y. Yoshida: *Hyperfine Int.*, **35** (1989), 807.
- (48) H. B. Huntington: private communication to Slifkin, (1958).
- (49) M. Koiwa and S. R. MacEwen: *Philos. Mag.*, **26** (1972), 173.
- (50) M. Arita, M. Koiwa and S. Ishioka: *Trans. JIM*, **29** (1988), 439.
- (51) M. Koiwa: *Ordered Intermetallics—Physical Metallurgy and Mechanical Behaviour*, Ed. by C. T. Liu, R. W. Cahn and G. Sauthoff, Kluwer Academic Press, (1992), 449.
- (52) P. Wynblatt: *Acta Metall.*, **15** (1967), 1453.
- (53) M. Arita, M. Koiwa and S. Ishioka: *Acta Metall.*, **37** (1989), 1363.
- (54) J. P. Neumann, Y. A. Chang and H. Ipsen: *Scripta Metall.*, **10** (1976), 917.
- (55) A. Lutze-Birk and H. Jacobi: *Scripta Metall.*, **9** (1975), 761.
- (56) Y. Mishin and D. Farkas: *Philos. Mag. A*, **75** (1997), 187.
- (57) J. Mayer and M. Fähnle: *Defect Diffusion Forum*, **143** (1997), 285.
- (58) M. Arita, M. Koiwa and S. Ishioka: *Philos. Mag. A*, **60** (1989), 563.
- (59) C. R. Kao and Y. A. Chang: *Intermetallics*, **1** (1993), 237.
- (60) I. V. Belova and G. E. Murch: *Intermetallics*, **6** (1998), 115.
- (61) I. V. Belova and G. E. Murch: MRS Symposium 'Diffusion Mechanisms in Crystalline Materials,' San Francisco, April 1998.
- (62) N. A. Stolwijk, M. van Gend and H. Bakker: *Philos. Mag. A*, **42** (1980), 783.
- (63) H. Bakker, N. A. Stolwijk and M. A. Hoetjes-Eijkel: *Philos. Mag. A*, **43** (1981), 251.
- (64) R. Kikuchi and S. Sato: *J. Chem. Phys.*, **51** (1969), 161; **57** (1972), 4962.
- (65) H. Bakker: *Philos. Mag. A*, **40** (1979), 525.
- (66) F. M. d'Heurle and P. Gas: *J. Mater. Res.*, **1** (1986), 205.
- (67) M. Koiwa and S. Ishioka: *Philos. Mag. A*, **48** (1983), 1.
- (68) T. Ito, S. Ishioka and M. Koiwa: *Philos. Mag. A*, **62** (1990), 499.
- (69) H. Numakura, T. Ikeda, M. Koiwa and A. Almazouzi: *Philos. Mag. A*, **77** (1998), 887.
- (70) H. Yasuda, H. Nakajima and M. Koiwa: *Defect Diffusion Forum*, **95–98** (1993), 823.
- (71) K. Nonaka, T. Arayashiki, H. Nakajima, A. Almazouzi, K. Tanaka, T. Ikeda, H. Numakura and M. Koiwa: *Defect Diffusion Forum*, **143–147** (1997), 269.
- (72) M. Koiwa, H. Numakura and S. Ishioka: *Defect Diffusion Forum*, **143–147** (1997).
- (73) G. F. Hancock: *Phys. Stat. Sol. (a)*, **7** (1971), 535.
- (74) S. Maeda, K. Tanaka and M. Koiwa: *Defect Diffusion Forum*, **95–98** (1993), 855.
- (75) S. Maeda: Master thesis, Graduate School of Engineering, Kyoto University, (1993).
- (76) N. Kurita and M. Koiwa: to be published.
- (77) T. Ikeda, A. Almazouzi, H. Numakura, M. Koiwa, W. Sprengel and H. Nakajima: *Acta Mater.*, **46** (1998), 5369.