Part I

Diffusion Mechanisms in Metals and Alloys

DIFFUSION IN METALS, QUASICRYSTALS, AND INTERMETALLIC COMPOUNDS

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ABSTRACT

In this paper recent developments of diffusion in three related areas will be reviewed: The first part is devoted to self- and solute diffusion in metals with particular emphasis on Al. Contrary to most other metallic solvents, diffusion of transition elements in Al is anomalous in several respects: diffusion is very slow, activation enthalpies, pre-exponential factors and activation volumes are unusually high. By contrast, non-transition elements in Al show more or less normal solute diffusion behaviour. The anomalous behaviour is attributed to a strong repulsive interaction between transition metal solutes and vacancies. Ab-initio calculations could help to understand this well-documented diffusion problem in detail.

In the second part very recent diffusion studies on single crystals of the Al-base quasicrystalline intermetallic compound Al-Pd-Mn will be discussed. Diffusion of Zn, Ge, Mn, Fe, Co, Pd and Au has been studied by various groups. At least in the high-temperature regime diffusion in the quasicrystal – despite some differences in detail – shows striking similarities to diffusion in Al, for which a vacancy-type mechanism is generally accepted. The activation volumes of +0.67 and +0.74 atomic volumes measured for Mn- and Zn-diffusion in Al-Pd-Mn strongly favour a vacancy mechanism as well. For the low temperature regime of Pd and Au diffusion the possibility of a phason-related mechanism is discussed.

The third part deals with recent investigations of iron-aluminides and iron-silicides for which Fe self-diffusion and diffusion of selected foreign elements (Ge in Fe–Si, In and Zn in Fe–Al) has been investigated. There is no doubt that vacancies mediate the diffusion process. Within this general mechanism a number of factors like the crystal structure, the state of order, the composition, and the type of bonding have strong influence on diffusion. Such factors are discussed also in connection with results from positron annihilation and Mössbauer spectroscopy.

DIFFUSION IN METALS

Self-diffusion

Diffusion coefficients in solids normally follow an Arrhenius form which is written empirically as

$$D = D^0 \exp\left(-\frac{Q}{RT}\right), \tag{1}$$

where D^0 is called pre-exponential factor and Q activation enthalpy for diffusion. R denotes the ideal gas constant and T the absolute temperature. Usually self-diffusion in metals is characterized by Q- and D^0-values which fall in the following ranges (see, e.g., [1, 2, 3]):

$$Q = (17\,\mathrm{to}\,18)RT_m, \;\; 10^{-6}\mathrm{m}^2\mathrm{s}^{-1} \le D^0 \le 10^{-3}\mathrm{m}^2\mathrm{s}^{-1}. \tag{2}$$

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	Cu	Ag	Au	Al
$\Delta V/\Omega$ for self-diffusion	0.9 to 1.0	0.65 to 0.9	0.72 to 0.78	1.29
$\Delta V/\Omega$ for impurities	Au: 0.92, Zn: 0.85	In: 0.81, Sb: 0.77		see below

Table 1: Activation volumes of self- and impurity diffusion for some fcc metals in units of the atomic volume Ω of the matrix metal.

These values lead to self-diffusivities near the melting temperature T_m between 10^{-12} and $10^{-11}\text{m}^2\text{s}^{-1}$. Fig. 1 shows an Arrhenius plot of self-diffusion of several face centred cubic (fcc) metals in a temperature scale normalized with T_m (for references see [2]). We emphasize that Al complies well with these rules.

Careful dilatometric, quenching and annealing experiments, and positron annihilation studies indicate vacant lattice sites as being the defects responsible for self-diffusion. Fig. 2 shows an illustration of the wellknown vacancy mechanism which we dare to show since this is the first contribution in the first session of a symposium on 'diffusion mechanisms'. For temperatures up to 0.7 T_m the monovacancy is the defect which is responsible for self-diffusion. At temperatures above 0.7 T_m some additional small contribution of divacancies (see also Fig. 2) which varies from metal to metal occurs (see, e.g., [5, 6, 7]). For reasons of simplicity we neglect this contribution in the following.

For self-diffusion via vacancies the activation enthalpy and pre-exponential factor have the meanings

$$Q = H^F + H^M, \; D^0 = fa^2\nu_0 \exp\left(\frac{S^F + S^M}{R}\right). \tag{3}$$

H^F and H^M are formation and migration enthalpies of the vacancy and S^F and S^M are the corresponding entropies. f denotes the correlation factor, a the lattice parameter, and ν_0 the attempt frequency (of the order of the Debye frequency).

From diffusion studies performed under hydrostatic pressure p an activation volume ΔV of diffusion can be deduced according to

$$\Delta V = -RT \cdot \left(\frac{\partial \ln D}{\partial p}\right)_T + \text{small corr. term.} \tag{4}$$

The activation volume of self-diffusion

$$\Delta V \; = \; V^F + V^M \tag{5}$$

is the sum of the formation volume V^F and the migration volume V^M of a vacancy in the pure solvent. The pressure dependence of diffusion in metals has been reviewed recently by one of the present authors [8]. Values for the activation volumes of self-diffusion in fcc metals are summarized in Table 1. Self-diffusion is characterized by values between about 0.65 and 1.29 atomic volumes Ω which are characteristic of a vacancy-type diffusion mechanism.

Normal impurity diffusion

For metals containing a sufficiently small amount of solute concentration diffusion can be considered in terms of isolated atoms. Then we talk about impurity diffusion and denote the diffusivity by D_2. Examples of 'normal' impurity diffusion are given in Fig. 3 which shows

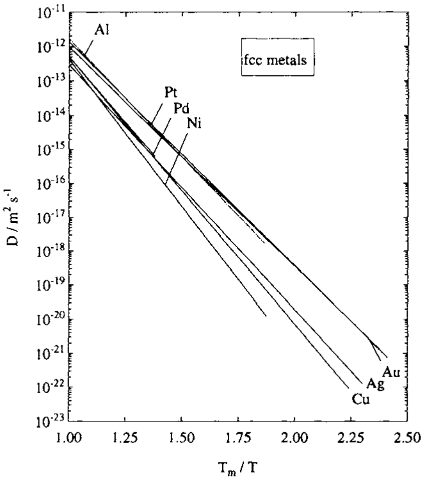

Figure 1: Self-diffusion of several fcc metals versus reciprocal temperature normalized by the melting temperature.

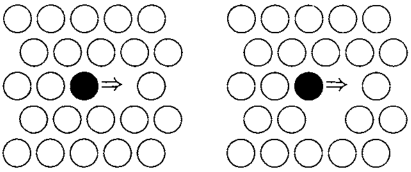

Figure 2: Vacancy and divacancy mechanism of diffusion.

diffusion for several solutes in Cu together with Cu self-diffusion. D_2 values do not differ significantly from self-diffusion and the pre-exponential factors and activation enthalpies of diffusion obey the inequalities

$$0.1 < \frac{D^0(solute)}{D^0(self)} < 10 \quad \text{and} \quad 0.75 < \frac{Q_2}{Q} < 1.25. \tag{6}$$

Diffusion of substitutional solutes in most other thoroughly studied fcc solvents like Ag, Au, and Ni comply with the rules in 6 (see chapter 3 in [2] and [12] for references). When the vacancy mechanism is operating the appropriate expression for the diffusion coefficient of an impurity is

$$D_2 = f_2 a^2 \omega_2 C_V \exp\left(\frac{G^B}{RT}\right). \tag{7}$$

Here f_2 is the correlation factor of impurity diffusion and C_V^{eq} the equilibrium vacancy concentration in the pure solvent. $G^B = H^B - TS^B$ denotes the Gibbs free energy of binding of the vacancy-impurity complex and ω_2 the vacancy-impurity exchange frequency. The product $C_V \exp(G^B/RT)$ is sometimes also denoted as vacancy availability factor of the impurity. The activation enthalpy of impurity diffusion is given by [1, 2, 3]

$$Q_2 = H^F - H^B + H_2^M - C, \tag{8}$$

where the correlation term C accounts for the temperature dependence of f_2 and H_2^M is the enthalpy of the vacancy-impurity exchange jump.

Normal impurity diffusion is rather well understood in terms of the so-called electrostatic model [9, 10] and its modifications [11]. As pointed out by Le Claire, the relative values

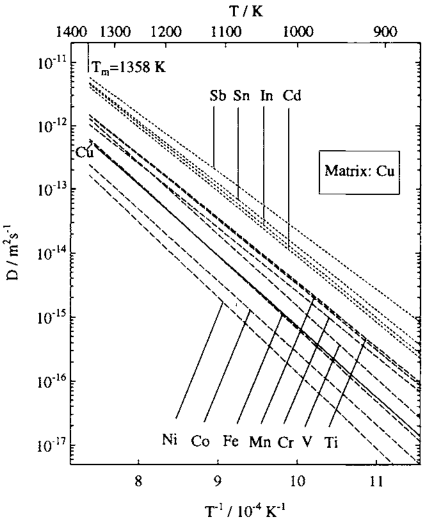

Figure 3: Diffusion of several solutes and self-diffusion in Cu.

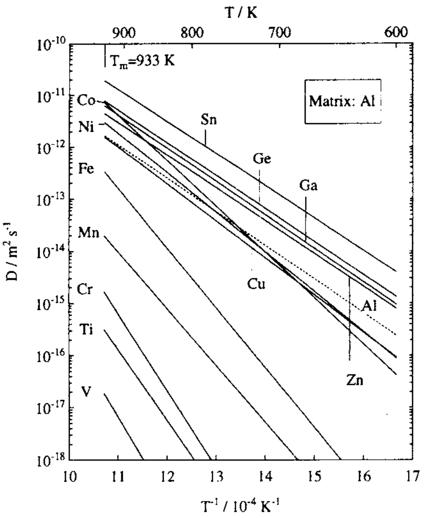

Figure 4: Diffusion of several solutes and self-diffusion in Al.

of D_2 and D are largely determined by $\Delta Q = Q_2 - Q$. When $D_2 > D$ the impurity is a faster diffuser than the host and ΔQ is negative. It is often found that this is correlated to a situation where the valence of the impurity is greater than that of the host.

In a few cases activation volumes of normal impurity diffusers (e. g.: Au and Zn in Cu, In and Sb in Ag) have been studied as well. The values fall into the same range as the activation volumes of self-diffusion as can be seen from Table 1 (see [8] for references). Their magnitudes confirm a vacancy-type mechanism for diffusion of substitutional solutes.

Anomalous impurity diffusion in Al

The temperature and pressure dependence of diffusion of several solutes in pure Al has been recently reconsidered in our laboratory (Au, Zn [13, 20], Sn [14, 15], Cr, Mn, Fe, Co [16, 17], and Ge [18]). Oxide hold-up effects of the isotope at the surface, which were often encountered in earlier tracer diffusion studies of Al and Al-base alloys, have been overcome either by sputter-cleaning of the diffusion samples or by implantation of the radioisotope. The results for the temperature dependence are summarized in Fig. 4. The following empirical facts are well established:

Non-transition element solutes in Al like Ge, Sn, Ga, Zn are 'normal' diffusers in the sense defined above (see Fig. 4). Activation enthalpies of 'normal' diffusers in Al are not much different from the activation enthalpy of Al self-diffusion. Activation volumes of self-diffusion and activation volumes of non-transition element solute diffusers are either slightly below or slightly above one atomic volume as can be seen from the collection of ΔV values shown in Fig. 5 (for references see [8]).

Transition element solutes in Al are 'anomalous' slow diffusers. Their diffusivities depend strongly on the number of 3d-electrons and decrease in the sequence Co, Fe, Mn, Cr, Ti, and V (see Fig. 4). Their activation enthalpies are significantly larger than that of self-diffusion. Q_2 increases in the sequence Co, Mn, Fe, Cr, and V. Their pre-exponential factors are large and their activation volumes (see Fig. 5) are considerably larger than one atomic volume too.

The theoretical clue for the remarkable differences between transition element and non-transition element diffusers in Al lies in the vacancy-solute interaction. Large Q_2 values of transition element solutes according to (8) indicate a strong repulsion between solute and vacancy ($H^B < 0$) and/or a large activation enthalpy H_2^M for solute-vacancy exchange.

The application of the electrostatic model [9] to the diffusion of transition elements in Al by Hood [19] appeared to be quite successful, when potentials with Friedel oscillations instead of Thomas-Fermi potentials were used. The conclusion was that for transition element solutes the solute-vacancy interaction is strongly repulsive at the saddle-point of the vacancy-solute exchange and very likely also repulsive at the nearest neighbour position. However, later on Beke et al. [23] considered several oscillatory screening potentials for impurities in Al and found significant differences in the predicted ΔQ-values.

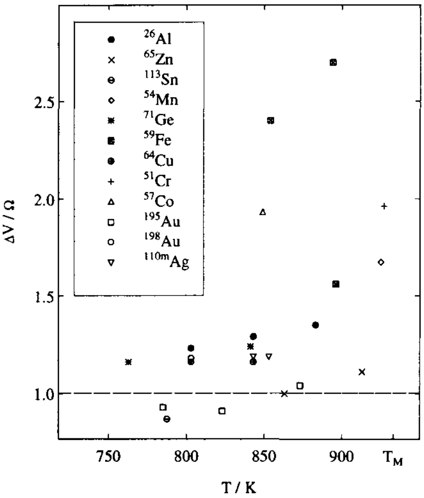

Figure 5: Activation volumes for diffusion in Al according to [8].

The symposium on 'Diffusion mechanisms in crystalline materials' brought great progress in the understanding of diffusion mechanisms in solids through the application of modern methods of computational materials science [24]. Vacancy-impurity binding energies, migration energies and activation volumes of impurities in Al are waiting for such applications. Ab-initio calculations based on local density functional theory should be able to make a strong impact on this relatively old problem. From an experimental point of view we note that for Al by far the largest database of D_2-, Q_2- and ΔV-values exists as compared to other metals.

DIFFUSION IN QUASICRYSTALLINE Al-Pd-Mn

Quasicrystals (QCs) can be considered as a class of intermetallic compounds which violate canonical rules of classical crystallography. QCs exhibit many unusual physical properties. Examples are the low electronic and thermal conductivity, the low density of states at the Fermi-level and unusual optical properties. High hardness, low friction and good oxidation and corrosion resistance are further characteristics (see, e. g., [25, 26, 27]). Unfortunately, QCs have in common with other intermetallics that they are brittle at room temperature which up to now limits applications to quasicrystalline coatings. QCs become plastic at elevated temperatures and show the phenomenon of deformation softening. The latter has been attributed to phason creation by moving dislocations and the associated disordering [28].

The established list of unusual physical properties of QCs also raises the question whether their diffusion behaviour is also unusual. Kalugin and Katz [30] have indeed proposed a novel mechanism of diffusion which is unique to QCs. This mechanism is based on specific geometric properties of the quasicrystalline structure and the necessity that matching rules have to be obeyed to build up a perfect quasiperiodic lattice. Matching-rule violations are called *phason defects*. So-called phason-flips cause atomic jumps with low activation energies. Kalugin and Katz discuss the possibility that the ‘phason mechanism’ could dominate over the vacancy mechanism and they suggest a strongly non-linear Arrhenius plot of diffusion coefficients in QCs. Because of the general nature of their considerations, they were neither able to determine at which temperature these deviations are to be expected nor to estimate their order of magnitude. Since the work of Kalugin and Katz, further theoretical work on phason-related diffusion in QCs has been published [31, 32, 33].

The *phason mechanism* is illustrated in Fig. 6 for the example of a two-dimensional octagonal tiling. The sequence of phason-flips in Fig. 6 can be considered either as local violations of matching rules in the model of a perfect QC or as an example of dynamics in the octagonal random tiling model. This process returns the system to its initial state and gives rise to a cyclic permutation of points 1, 2, and 3.

The phason mechanism resembles the so-called *ring mechanism* of diffusion proposed for crystalline solids already in the 20s by the American metallurgist Zay Jeffries [40] and later on advocated in the 50s by Zener [34]. The ring mechanism also leads to a cyclic permutation of 4 (or more) atoms. Both mechanisms have in common that vacancies are not involved.

The idea of *non-defect mechanisms*, such as the direct exhange of two neighbouring atoms or ring exchanges, had been abandoned in the diffusion literature, when it became evident that vacancies are responsible for self-diffusion and diffusion of substitutional solutes in metals in practically all cases [35]. There is, however, some renewed interest in non-defect mechanisms of diffusion in connection with the enhanced diffusivity near phase transitions [36, 37]. In addition for substitutionally dissolved B in Cu there is evidence from β-NMR experiments for a non-defect mechanism of diffusion [38].

The first metastable QCs were discovered in the mid 80s in Al-rich transition metal alloys [29]. The discovery of thermodynamically stable quasicrystalline phases [39] made it possible to apply conventional crystal growth techniques to the growth of QCs. Nowadays it is possible to grow large single-crystals for a few QCs. Icosahedral Al-Pd-Mn is perhaps the best example.

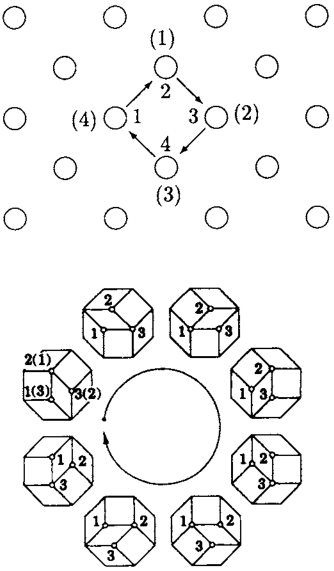

Figure 6: Bottom: Phason mechanism in quasicrystals illustrated for an octagonal tiling model. Top: Ring mechanism of diffusion in crystals.

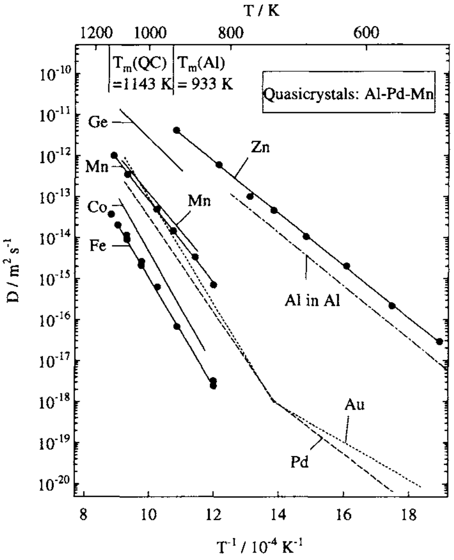

Figure 7: Diffusion in icosahedral monocrystalline QCs of Al-Pd-Mn. For references: 1 [40, 41], 2 [42, 43, 44, 45], 3 [47], 4 [48].

Until recently experimental studies of diffusion in QCs were extremely scarce. The few literature data before 1996 were obtained exclusively on polycrystalline samples. Some unusual features of Mn-diffusion reported in one of these earlier experiments which were originally felt to be specific to the quasicrystalline structure were later on attributed to imperfect polycrystalline material [43].

In Fig. 7 we concentrate on diffusion in monocrystalline QCs of icosahedral Al-Pd-Mn (approximate composition of the QC phase $Al_{70.4}Pd_{21.2}Mn_{8.4}$): The first published study on single crystals were measurements of ^{54}Mn and ^{59}Fe diffusion from our laboratory in Münster [41, 42]. Our data were confirmed at the same time in Japan by Sprengel et al. [43] in a further study of Mn-diffusion. The same group in the meantime also studied diffusion of ^{68}Ge and ^{60}Co [45, 46, 47]. Diffusivities of implanted ^{103}Pd and ^{195}Au between 543 and 1083 K were reported by the Stuttgart group [48]. The authors represent their measurements by different Arrhenius laws above and below 723 K with extremely low activation energies and pre-exponential factors for the low-temperature regime. Very recently, diffusion of ^{65}Zn was studied in our laboratory over the temperature range 528 to 923 K [49]. No deviation from linear Arrhenius behaviour was observed although the investigated temperature range is even wider than the one investigated in [48].

The base metal of most quasicrystalline compounds is Al. Therefore it may be interesting to compare diffusion in Al-Pd-Mn QCs with diffusion in pure Al discussed above:

Al self-diffusion has been studied so far only in Al and not in Al-Pd-Mn QCs. This gap is due to the lack of an affordable radioisotope for Al. The non-transition elements Zn and Ge are relatively fast diffusers in both Al and Al-Pd-Mn QCs. In pure Al their diffusivities are not much different from Al self-diffusion (see Fig. 4) suggesting that Al diffusion in the QC also occurs with similar rates. Mn, Fe, and Co are relatively slow diffusers in both Al-Pd-Mn QCs and in Al and their activation enthalpies and pre-exponential factors are large in both materials. Some details like the sequence of diffusivities of the transition elements in Al and Al-Pd-Mn QCs are different.

The diffusion data of icosahedral Al-Pd-Mn QCs discussed so far reveal many similarities to diffusion in Al. For self- and impurity diffusion in Al the vacancy is the generally accepted defect which mediates diffusion. It is therefore natural to conclude as we have already done previously [41, 42] that bulk diffusion in Al-Pd-Mn QCs at least in the high temperature range occurs by a vacancy mechanism [41, 42]. This conclusion is strongly supported by the activation volumes

$$\Delta V(Mn) = +0.67\,\Omega \quad \Delta V(Zn) = +0.74\,\Omega. \tag{9}$$

These values were obtained from the pressure dependence of ^{54}Mn diffusion at 1023 K and of ^{65}Zn diffusion at 776 K for Al-Pd-Mn QCs in our laboratory [42, 49]. Ω denotes the mean atomic volume of Al-Pd-Mn. Magnitude and sign of the activation volumes comply well with vacancy diffusion (see Table 1).

Diffusion of Pd and Au above 723 K has been explained by Blüher et al. [48] also in terms of a vacancy mechanism. By contrast, diffusion below 723 K and the associated low values of pre-exponential factors and activation enthalpies of Pd and Au were attributed to a phason-related mechanism. On the other hand, in the work of Blüher et al. the tracer atoms were implanted before the samples were diffusion annealed. Implantation causes radiation damage which might enhance diffusivities especially at lower temperatures where the average diffusion lengths are not much different from the implantation depths. In our opinion further experiments are needed to check the possible influence of implantation damage.

In our work on Zn diffusion the tracer was deposited onto the surface by evaporation. The Zn diffusivity follows a linear Arrhenius relation over the whole temperature range which is even wider than the one for Pd and Au. On the other hand, the Zn diffusivity at the lowest temperature investigated is still higher than the Pd or Au diffusivity at 723 K (see Fig. 7).

We will not speculate about the origin of the different behaviour of Zn diffusion on the one hand and Pd and Au diffusion on the other hand. The heterogeneity of Al-Pd-Mn QCs with an Al substructure and a Pd substructure might or might not be a reason for this difference. In our opinion there is strong evidence for vacancy-mediated diffusion in QCs. A clearcut identification or rejection of phason-related diffusion has to wait for further good experiments. We should keep in mind that the field of diffusion in crystalline materials has been given the time to mature over several decades. We are now just beginning to understand the basic features of diffusion in quasicrystals.