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A review on bulk diffusion in metallic solids

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Abstract

In this paper bulk diffusion techniques in case of metals and alloys will be reviewed with a special emphasis on resistometric technique. The experiment is restricted only to those metals, which can be made in the form of wire but has the advantage of applying to materials whose suitable radioactive isotopes are not available. A brief introduction along with different diffusion mechanisms with corresponding activation energies, diffusion coefficients, correlation factors, isotope effect, enhancement factor, etc. is also incorporated. Three models for bulk diffusion are also mentioned.

1 Introduction

The perfect crystal has an infinite three dimensional repetition of identical units while real crystals are limited in size containing some disorder in stacking, called defects. Many of the interesting properties of solids are controlled by them which include the electronic structure reflected in optical and spin resonance data, formation energies, and diffusion parameters. Defects represent singularity in an otherwise perfect crystal and these singularities are accompanied by localized increase of internal energy relative to that of the perfect crystal. Of course the concept of defects is used only when concentration of such defects is small; otherwise the crystalline reference state loses its unique identity. Most of them occur as a result of atomic migration through the solids (e.g. diffusion phenomena, sintering, electrolytic conduction and solid state chemical reaction). However out of all these phenomena, diffusion phenomena are the predominant one and so the understanding of the matter transport through solids via diffusion phenomena is of great importance. The theory of diffusion is based on the idea of atomic jump from one lattice site to another. One can calculate the frequencies of these jumps and correlates them with diffusion parameters. Atoms in a crystal oscillate around their equilibrium positions and occasionally these oscillations become violent to allow an atom to change sites. It is these jumps from one site to another which gives rise to diffusion in solids. First an elementary survey of the diffusion mechanisms [1-4] will be given.

2 Mechanisms of diffusion in bulk samples

In thermal equilibrium at a temperature above absolute zero, a crystal will contain a certain concentration of vacant lattice sites. An atom adjacent to a vacancy may jump into the

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vacancy producing diffusion by vacancy mechanism (figure 1). This is the simplest case. If the atoms in the region of a vacancy relax inward into the vacant lattice to such an extent that the regular lattice structure in this region out of several atom distances disappears, the resulting region is called relaxed region. When a binding energy exists between vacancies a fraction of vacancies in the form of bound vacancy pairs (known as divacancies) may be obtained. Diffusion by means of divacancies may in certain materials be appreciable at high temperatures. The vacancy mechanism is well established as the dominant mechanism of diffusion in most pure fcc metals and alloys and has been shown operative in many bcc and hcp metals as well as in ionic compounds and oxides.

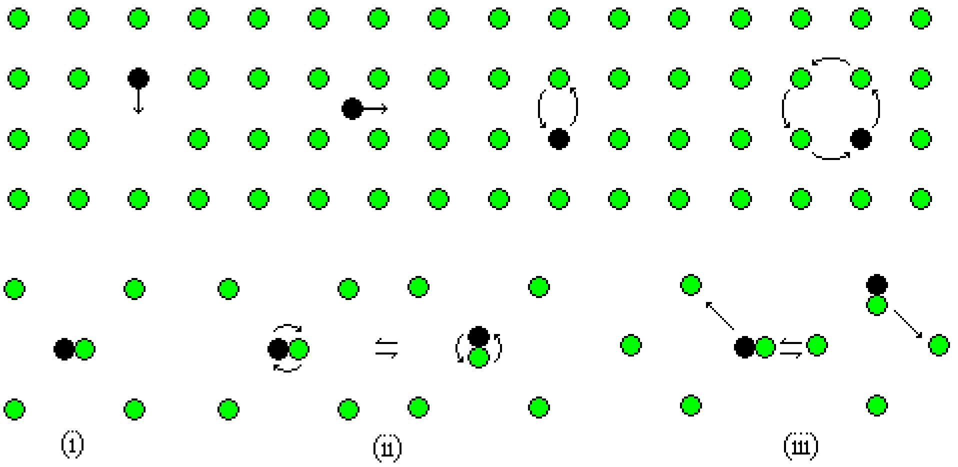

Figure 1 Vacancy mechanism; Interstitial mechanism; Exchange and Ring mechanism of diffusion; Diplon mechanism of diffusion model - (i) single diplon, (ii) reorientation of diplon and (iii) diplon motion.

Some atoms may occupy interstitial positions in the crystal lattice and may jump into a near neighbouring interstitial site without permanently displacing any of the matrix atoms. This is direct interstitial mechanism. This mechanism is particularly likely for diffusion of small impurity atoms, which easily fit into interstitial sites and during movement do not greatly displace the solvent atoms from their normal lattice sites. When the interstitial atom is nearly equal in size to the lattice atoms, diffusion is more likely to occur by the interstitialcy mechanism. Here the interstitial atom does not move directly to another interstitial site. Instead it moves into a normal lattice site and the atom, which was originally at the lattice site, is pushed into a neighbouring interstitial site. Thus it prevents an appreciable local distortion of the neighbouring lattice atoms. A third type of interstitial configuration is the crowdion. Here the additional atom is introduced into a more or less close packed row of atoms. Each atom in the row, to perhaps ten atom distances from the additional atom, is displaced somewhat from the equilibrium lattice positions. The crowdion configuration can move along this row. In passing down a row from one end to the other the crowdion displaces each atom in the row one atom distance. In some cases interstitialcy is centered on a lattice site and two atoms occupy this site symmetrically in a dumbbell like configuration, each being displaced by an equal amount from the normal lattice position.

A pair of neighbouring atoms may exchange places, or a ring of atoms may rotate about a common center (figure 1). These mechanisms are unlikely in crystals with tightly packed atom structures since each atom in this case closely surrounded and hemmed in by its neighbours. The atoms need to be considerably compressed before they could squeeze past one another and interchange positions. These mechanisms may be possible in very loosely packed crystals (bcc lattice).

Let two atoms be paired at a single substitutional position of a structure. They may be composed of host-host, host-impurity, or impurity-impurity atoms, and offered the designation diplon [5]. Diplon has only rotational symmetry about its axis. Diffusive transport can occur by the reorientation of the diplon and jumping of one of the atoms of the diplon to an adjacent atom (figure 1). The formal theory for diffusion by this mechanism, as well as for the equilibrium between the diplon and other impurity states, is the same as for the conventional interstitials. Since either atom of a host-host diplon can remain at the lattice, when the diplon moves on, such a defect move essentially like a self-interstitial. An impurity-impurity diplon, on the other hand, must perform some sort of exchange with neighbouring host atoms if it is to move. If it is tightly bound as well, its mechanism of motion must be somewhat similar to that of a substitutional impurity. However, the reorientation of the diplons, are not necessarily capable of producing diffusion. Finally there is the host-impurity diplon, which might move by a vacancy mechanism, but will be most interesting when it does not. Then in structures with closed interstitial voids, in the sense that the energy barriers to passage out of a given void through its various faces are all approximately equal, neither a diplon motion by translation of the impurity atom nor a rotation of the diplon about its lattice is sufficient to cause net diffusion of the impurity atom. Both are required or else a single motion, which produces the effects of both is required, if the impurity is to show any long range motion. Furthermore, if the barriers to the appropriate motions are not too high the resulting diffusion can be very fast [6].

The above mechanisms are concerned with diffusion in regions where the regular lattice structure breaks down. They involve line or surface discontinuities in the crystal. It is clear that diffusion should occur more easily in the open regions of the crystal at dislocations, grain boundaries and surfaces. However, the detailed atomic paths in each case will depend on the particular atomic configurations at each line or surface defect. Thus these mechanisms do not lend themselves easily to the detailed kinetic analysis. Since the number of dislocations, grain boundaries and surfaces is more or less independent of temperature, diffusion by these mechanisms might be expected to have smaller temperature dependence than that for mechanisms involving point defects whose concentration increases with temperature. Line and surface mechanisms are relatively important at low temperatures but usually are not so important at high temperatures.

3 Defect formation, Motion and Diffusion Coefficient

All the diffusion mechanisms are thermally activated. So at thermal equilibrium the probability of an imperfection being at a given site is proportional to a Boltzman factor $e^{-E_f/RT}$ where E_f is the defect formation energy, R the universal gas constant and T the absolute temperature. Due to thermal energy when an atom jumps into a neighbouring site for any type of mechanism, the path of its motion passes through a region of maximum energy. This is the saddle point or activated position. The difference between the Gibbs' free energy of the crystal when the atom is at a lattice site can be related to the jump frequency as $\nu_m = \nu(0)e^{-E_m/RT}$. Here $\nu(0)$ is the vibration frequency of an atom about its equilibrium position in the jump direction and E_m the defect migration energy. For a defect mechanism the jump frequency of an atom to a given neighbouring site is simply the product of jump frequency ν_m if the defect is in the given site and the probability of a defect being at that given site. If there are n near neighbours around the defect the total jump frequency ν is given by $\nu = n\nu(0)e^{-Q/RT}$, where $Q = E_f + E_m$ is the activation energy for diffusion. Since no defect is required for diffusion by exchange or ring mechanism E_f equals zero there.

The diffusion coefficient D can be defined from the proportionality condition of flux of atoms per unit area in a specified direction ($\vec{J}$) and the concentration gradient at that direction ($\vec{\nabla} c$), which is Fick's first law or $\vec{J} = -D\vec{\nabla} c$. A minus sign appears because the flux usually is in the direction of decreasing concentration. Combining it with the continuity condition we get Fick's second law or $(\partial c/\partial t) = -\vec{\nabla} \cdot (D\vec{\nabla} c)$. This differential equation may be solved for various boundary conditions.

Three types of diffusion coefficients may be defined. (i) Tracer diffusion coefficient is the basic and is directly related to the atomic jump frequencies in an otherwise homogeneous crystal. (ii) Intrinsic diffusion coefficient is obtained when some driven forces are present. (iii) Interdiffusion coefficient depends on rate of mixing of two different elements. However, we shall consider only the first one where the tracer atoms may be of same kind (self diffusion) or different (impurity diffusion). Self and impurity diffusion coefficients obey temperature dependent Arrhenius equation $D_S = D_0 e^{-Q_0/RT}$ and $D_I = D_2 e^{-Q_2/RT}$. Here 0 and S refers to the pure solvent and the subscripts 2 and I apply to a solute property. D_0 and D_2 are the pre-exponential factors and, Q_0 and Q_2 are the corresponding activation energies.

4 Correlation factor

Diffusion takes place by the diffusing atom following a series of jumps from site to site. If the jumps are random the path followed by each atom during diffusion may be described as a random walk. The random walk equations apply strictly to diffusion by an interstitial mechanism, but with appropriate correlation factor may be applied to diffusion by other mechanisms. Applying the position probability and Einstein diffusion equation, we obtain the diffusion coefficient as $D = r^2 \nu f/6$, where r is the jump distance, ν the jump frequency and f the correlation factor defined as $f = 1 + 2\sum_i < \cos\theta_i >$, $\cos\theta_i$ being the cosine of the angle between the first jump and the ith following jump. The value of $< \cos\theta_i >$ is not always zero and for vacancy mechanism $< \cos\theta_i > = < \cos\theta >^i$ and so $f = (1 + < \cos\theta_1 >)/(1 - < \cos\theta_1 >)$. For self diffusion in cubic metals the probability of jump is a numerical constant independent of temperature, i.e. $f_0 = 0.78146$ (for, e.g., fcc metals). The probability for impurity diffusion depends on relative jump frequencies of the neighbouring solvent atoms relative to the values in absence of the impurity. After an impurity-vacancy exchange the vacancy may either re-exchange with the impurity atom or exchange with a neighbouring solvent atom. Even after the solvent-vacancy exchange the vacancy may eventually return and exchange with the impurity and also it may happen for other solvent sites. So partial correlation factor, (f_p) can be taken into consideration for the effective escape frequency. f_p is the fraction of vacancies making ν_3 jumps that effectively do not return to the site from which the ν_3 jump was made (figure 2). So the final expression for impurity correlation factor is

$$f_2 = \frac{2\nu_1 + 7 f_p \nu_3}{2\nu_1 + 2\nu_2 + 7 f_p \nu_3} \tag{1}$$

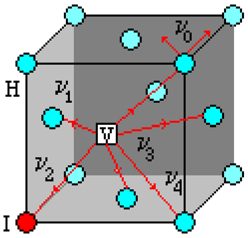

Figure 2 Vcancy jump frequencies in the vicinity of the impurity [Pure FCC lattice atom (Blue circles), Substitutional impurity (Red circle), Vacancy (White square)].

When $\nu_4 << \nu_0$, $f_p = 1$; for $\nu_4 \approx \nu_0$, $f_p = 0.75$; and for $\nu_4 >> \nu_0$, $f_p = 0.29$. Since ν_1, ν_2 and ν_3 are of Arrhenius type so f_2 is a temperature dependent function. Lidiard [7], LeClaire [8] evaluated the correlation factor for different kind of mechanisms for self and impurity diffusion. Manning [9] has extended the derivation including the ν_4 jump. For the fcc lattice four different jump frequencies for the vacancy near an impurity atom may be defined. As shown in figure 2, ν_1 is the frequency of exchange of a vacancy neighbouring an impurity atom with any of the four solvent atoms those are also neighbours of the impurity; ν_2 is the frequency of exchange of the vacancy and the impurity atom; ν_3 is the frequency of exchange of a vacancy neighbouring an impurity with any of the seven solvent atoms adjacent to the vacancy but not neighbours of the impurity (dissociation jump); ν_4 is the frequency of association jump (reverse of a ν_3 jump) and all other jumps are assumed to take place with a frequency ν_0 which is the frequency of solvent-vacancy exchange. Serious impurity diffusion models must include these correlation effects. The difference in activation energy for impurity and self diffusion is also related to this temperature dependent correlation factor according to this relation.

$$\Delta Q = Q_2 - Q_0 = \Delta E_f + \Delta E_m - C \qquad (2)$$

Where $$C = R\frac{\partial \ln f_2}{\partial(\frac{1}{T})} \qquad (3)$$

ΔE_f is the difference between the formation energies of a vacancy in the near neighbour position to that of a solvent atom. ΔE_m is the change in migration energy for solute and solvent motion in the pure solvent. Two limiting cases for the calculation of C are possible:

Slow diffusion $f_2 \to 1 \Rightarrow C = 0$

Fast diffusion $f_2 \to 0 \Rightarrow C << 0$ (4)

Thus for slow diffusion a direct comparison of theory and experiment is possible, while for fast diffusion entropy contribution must be estimated. Fast diffusion is observed in polyvalent metals (Pb, Sn, In, Tl) or very electropositive metals (Li, Na, K) with monovalent, divalent or transition metal impurities. In fast diffuser systems the impurity diffusivity is some order of magnitude higher than the host diffusion and it increases with decreasing solubility.

5 Isotope effect

Correlation factors can be determined from isotope effect measurements. Two isotopes of a given element, because of their difference in mass will not have exactly the same diffusion coefficient. The mass difference causes their vibrational frequencies to differ.

According to classical rate theory the vibrational frequencies and hence the jump frequencies should be inversely proportional to the square root of masses. For two isotopes i and j of the same element we have $\nu_i / \nu_j = \sqrt{m_j / m_i}$. But for diffusion of substitutional atoms we wave to use the reduced mass, which includes the effects from masses of neighbouring atoms. These neighbouring atoms must move to allow a diffusing atom to pass through the saddle point in its jump. Also after the jump was made, these atoms may have moved to a slightly different location from that occupied before the jump. The introduction of reduced mass modifies the mass-frequency relation as

$$\frac{\nu_i}{\nu_j} - 1 = \Delta K[\sqrt{\frac{m_j}{m_i}} - 1] \quad (5)$$

Here ΔK is the fraction of the translational kinetic energy that is possessed by the jumping atom as it crosses the saddle point. Hence ΔK is bounded by zero and unity. For both isotopes and for same jump distance we have

$$\frac{D_i - D_j}{D_j} = \frac{\nu_i f_i - \nu_j f_j}{\nu_j f_j} = [1 + \frac{\nu_i (f_i - f_j)}{f_j (\nu_i - \nu_j)}] \frac{\nu_i - \nu_j}{\nu_j} \quad (6)$$

In special case where each jump vector lies along an axis of at least two or threefold symmetry as in cubic crystals the effective solvent jump frequencies for both isotopes are same because they are unaffected by the mass of atoms executing ν_2 jumps. So equation (6) can be written as

$$\frac{D_i - D_j}{D_j} = f_i \frac{\nu_i - \nu_j}{\nu_j} \quad (7)$$

Combining it with equation (5) we get

$$f_i \Delta K[\sqrt{\frac{m_j}{m_i}} - 1] = \frac{D_i}{D_j} - 1 \quad (8)$$

The value of ΔK can be assumed to be same for self and impurity diffusion. This quality of kinetic energy factor is supported by theoretical investigation on the basis of the dynamical theory of diffusion. Experimentally it was that ΔK_2 for impurity diffusion does not depend on the impurity mass.

6 Enhancement Factor

The presence of impurity atom may appreciably change the jump frequencies for solvent atoms neighbouring the impurity atom (i.e. $\frac{\nu_1}{\nu_0}$, $\frac{\nu_3}{\nu_0}$ and $\frac{\nu_4}{\nu_0}$ may be different from unity). Lidiard [10] was first to correctly derive the average solvent atom jump frequency in terms of various jump frequency ν_i's. Assuming that all solvent jumps have a correlation f_0 as in the pure solvent, the self diffusion in dilute alloys with solute concentration c_I can be expressed by

$$D_I(c_I) = D_S(1 + b_1 c_I) \quad (9)$$

Here subscripts I and S are for impurity and host diffusion respectively. Higher order terms of c_I, result from the overlapping of influence spheres of solute atoms with raising concentrations. Howard and Manning [11] reanalyzed this problem and removed the assumption that all solvent jumps occur with a correlation factor f_0. There are twelve types of solvent jumps near an impurity occurring with frequencies ν_1, ν_3 and ν_4, i.e. different from ν_0. Each of these twelve jumps has a partial correlation factor f_{pi}. There are four possibilities for ν_1 jump and seven for ν_3 jump (figure 2). The contribution from ν_4, jumps are just reverse of ν_3 jump and there are seven possible ν_4 jumps for every site neighbouring an impurity. The contribution of these jumps to the average effective jump frequency of the solvent atoms equals the jump frequency multiplied by the probability that a vacancy is created next to an impurity. When the impurity is absent the contribution to effective jump frequency is $12P_{v0}c_I(11 f_0 \nu_0)$. But for the presence of the impurity the contribution would be modified to

$$12P_{vI}c_I(4 f_{p1}\nu_1 + 7 f_{p3}\nu_3) + 12P_{v0}c_I(7 f_{p4}\nu_4 - 7 f_0\nu_0)$$

Here $P_{vI} = P_{v0}e^{-\Delta E_f / RT}$. ΔE_f has been defined earlier and P_{v0} is the probability that a site far from any impurity is occupied by a vacancy. This change to the jump frequency contribution for the presence of the impurity is related to the enhancement factor b_1 according to the relation

$$b_1 = -18 + \frac{7 f_{p4}\nu_4}{f_0\nu_0} + [\frac{4 f_{p1}\nu_1 + 7 f_{p3}\nu_3}{f_0\nu_0}]e^{-\frac{\Delta E_f}{RT}} \tag{10}$$

Here it is assumed that divacancies do not form and each impurity remains isolated from other impurities. The total numbers of associative jumps are same as dissociative jump numbers. So

$$\nu_3 = \nu_4 e^{\frac{\Delta E_f}{RT}} \tag{11}$$

and

$$b_1 = -18 + \frac{4 f_{p1}\nu_1\nu_4}{f_0\nu_0\nu_3} + \frac{7\nu_4}{f_0\nu_0}(f_{p3} + f_{p4}) \tag{12}$$

This is the expression for enhancement factor b_1 for FCC metals. Analogous relation exists for BCC solvent metals.

7 Different theoretical diffusion models : Indirect diffusion model

The difference between the activation energies for impurity and self diffusion ΔQ has been calculated by different theoretical approaches. The electrostatic theory first proposed by Lazarus [12] and later modified by LeClaire [13] has provided further insight into the diffusion process. However, this is an indirect phenomenological model. Here a very brief representation of LeClaire theory for impurity diffusion in FCC lattice will be given. It utilizes the five frequency model where the ratio for impurity and self diffusion coefficient can be written as

$$\frac{D_I}{D_H} = \frac{f_2\nu_2}{f_0\nu_0}e^{-\frac{\Delta E_f}{RT}} = \frac{f_2\nu_2\nu_4}{f_0\nu_0\nu_3} \tag{13}$$

Here ν_i's are related according to the relation

$$\frac{\nu_i}{\nu_0} = \frac{\nu_i(0)}{\nu_0(0)}e^{\frac{\Delta E_{m_i}}{RT}} \tag{14}$$

And

$$\Delta E_{m_i} = E_{m_i} - E_{m_H} \tag{15}$$

Especially, $\Delta E_{m_2} = \Delta E_m$ has been defined earlier in equation (3.10). E_{m_i}'s are migration energies for different kinds of jumps. We can calculate the temperature dependent correlation factor using above equations as

$$\frac{CD_0 e^{-\frac{C}{RT}}}{f_0 D_2} = \frac{(\Delta E_m - \Delta E_{m_1})e^{-\frac{\Delta E_m + \Delta E_{m1}}{RT}} + \frac{7}{2}(\Delta E_m - \Delta E_{m_3})e^{-\frac{\Delta E_m + \Delta E_{m3}}{RT}}}{[e^{-\frac{\Delta E_{m1}}{RT}} + \frac{7}{2}e^{-\frac{\Delta E_m}{RT}}]^2} \tag{16}$$

The term ΔQ can be determined by calculating ΔE_f, ΔE_m and other ΔE_{m_i}'s and finally C from equation (16). Calculations have been done using electrostatic interaction between impurity and vacancy from Thomas-Fermi potential when a vacancy is created and at saddle point configuration when a vacancy is migrated. Details of these different terms were given in LeClaire [13]. The disadvantage of this method is that experimental values of D_2 and D_0 must be used in the C determination.

8 Direct diffusion model

A direct calculation of ΔQ, has also been proposed in a thermodynamical model by Neumann [14-15]. Here it is assumed that the interaction energies of impurities and host atoms are additively composed of those of pure components. The melting temperatures are considered to be a measure for the binding of the pure metal and Morse function was used. The expressions used in this model calculation are

$$\frac{D_2}{D_0} = \sqrt{\frac{m_H T_I}{m_I T_H}}\, \frac{f_2 e^{-\frac{C}{RT}} e^{\frac{1.17\beta\Delta E_M}{RT_H}}}{f_0} \tag{17}$$

$$0.235Q_0[\frac{T_I}{T_H}-1] = \Delta E_M = \frac{\Delta E_F}{0.17} = \frac{\Delta E_{M_1}}{0.19} = -\frac{\Delta E_{M_3}}{0.16} \tag{18}$$

$$f_2 = \frac{e^{-E\Delta E_{M_1}} + 2.575 e^{-E\Delta E_{M_3}}}{e^{-E\Delta E_{M_1}} + 2.575 e^{-E\Delta E_{M_3}} + \sqrt{\frac{m_H T_I}{m_I T_H}} e^{-E\Delta E_M}}$$

$$C = \frac{\Delta E_M [0.81 e^{-E\Delta E_{M_1}} + 2.987 e^{-E\Delta E_{M_3}}]\sqrt{\frac{m_H T_I}{m_I T_H}} e^{-E\Delta E_M}}{[e^{-E\Delta E_{M_1}} + 2.575 e^{-E\Delta E_{M_3}}][(e^{-E\Delta E_{M_1}} + 2.575 e^{-E\Delta E_{M_3}}) + \sqrt{\frac{m_H T_I}{m_I T_H}} e^{-E\Delta E_M}]} \tag{19}$$

Where $E = \frac{1-\frac{\beta T}{T_H}}{RT}$, $\beta = -\frac{\partial(\frac{\mu}{\mu_0})}{\partial(\frac{T}{T_H})}$ and $T = 0.85T_H$. m_H and m_I are the masses and, T_H and T_I are the melting temperatures of the solvent and the impurity respectively. The factor β represents the temperature dependence of the shear modulus, μ_0 being the shear modulus at absolute zero. The advantage of this method is that it is independent of individual experimental errors in D_2 as well as in ΔQ. m_H and m_I are the masses and, T_H and T_I are the melting temperatures of the solvent and the impurity respectively. The factor β represents the temperature dependence of the shear modulus, μ_0 being the shear modulus at absolute zero. The advantage of this method is that it is independent of individual experimental errors in D_2 as well as in ΔQ.

9 Pseudopotential diffusion model

Uptil now the above mentioned two methods can explain the most of the diffusion phenomena in FCC lattice. However, the models are strictly applicable for monovalent metals; but for polyvalent metals the effect of exchange and correlation should be taken into consideration. The effect of relaxations of the neighbours during migration should also be considered. It is possible to include all of them using the framework of pseudopotential theory of Harrison [16] for the host and impurity atom. The expressions for ΔE_f, ΔE_m including ΔE_R (the relaxation effect) were formulated to account for ΔQ [17]. The total energy of a metal per ion consists of structure dependent and volume dependent terms. The structure dependent terms consist of ion-ion interaction, which is electrostatic energy term

(E_{es}) and ion-electron and electron-electron interactions, i.e. band structure term (E_{bs}). As all defect calculations are done at constant volume the change in structure factor due to formation or movement of defects is reflected in the associated change of energy parameter. The activation energy of self diffusion Q_0, which consists of E_{es}^H and E_{bs}^H (H denoting host atom) can be regrouped so that it is possible to separate out E_{fH}, E_{mH} and E_{RH} of the vacancy. Similarly Q_2 can be separated into three parts where form it is possible to find expressions for ΔE_f, $\Delta E_m^{'}$ and ΔE_R. So the modified form of ΔQ with its respective terms are given by [18,19]

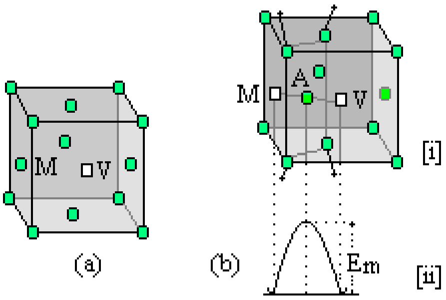

Figure 3 Diffusion via vacancy mechanism: (a) vacancy at V and migrating atom at near neighbour position M; (b) [i] activation state A for the migrating atom M with relaxation of four near neighbours around the activation state A, [ii] migration energy versus distance plot.

$$\Delta Q = \Delta E_f + (\Delta E_m^{'} + \Delta E_R) - C \tag{22}$$

Where
$$\Delta E_f = -\frac{z_H \Delta z e^2}{|\vec{r}_v - \vec{r}_I|} + \frac{\Omega_H}{\pi^2}\int_0^\infty \frac{\sin q|\vec{r}_v - \vec{r}_I|}{q|\vec{r}_v - \vec{r}_I|}[F_{HI}(q) - F_{HH}(q)]q^2 dq \tag{23}$$

$$\begin{aligned}\Delta E_m^{'} = {} & \sum_{q_0}{}' 2(\cos\vec{q}_0 \cdot \vec{r}_a - 1)[\underset{\eta\to\infty}{Lt}\frac{2\pi z_H \Delta z e^2}{\Omega_H q^2} e^{-\frac{q^2}{4\eta}} + F_{HI}(q_0) - F_{HH}(q_0)] + \underset{\eta\to\infty}{Lt}\, z_H \Delta z e^2 [\frac{2\sqrt{\eta}}{\sqrt{\pi}} \\ & + \frac{1}{|\vec{r}_v - \vec{r}_I|} - \frac{1}{|\vec{r}_I - \vec{r}_a|} - \frac{1}{|\vec{r}_a - \vec{r}_v|}] + \frac{\Omega_H}{\pi^2}\int_0^\infty [1 + \frac{\sin q|\vec{r}_v - \vec{r}_I|}{q|\vec{r}_v - \vec{r}_I|} - \frac{\sin q|\vec{r}_I - \vec{r}_a|}{q|\vec{r}_I - \vec{r}_a|} \\ & - \frac{\sin q|\vec{r}_a - \vec{r}_v|}{q|\vec{r}_a - \vec{r}_v|}][F_I(q) - F_H(q)]q^2 dq\end{aligned} \tag{24}$$

$$\begin{aligned}\Delta E_R = {} & z_H \Delta z e^2 \sum_{j=1}^{n}[\frac{1}{|\vec{r}_a - \vec{r}_j^{'}|} - \frac{1}{|\vec{r}_a - \vec{r}_j|}] + \frac{\Omega_H}{\pi^2}\int_0^\infty \sum_{j=1}^{n}[\frac{\sin q|\vec{r}_a - \vec{r}_j^{'}|}{q|\vec{r}_a - \vec{r}_j^{'}|} - \frac{\sin q|\vec{r}_a - \vec{r}_j|}{q|\vec{r}_a - \vec{r}_j|}] \\ & \times [F_I(q) - F_H(q)]q^2 dq\end{aligned} \tag{25}$$

z_H is the valency of this solvent metal, Δz the valency difference between solvent and solute, Ω_H the atomic volume, η the convergence factor, e the electronic charge, F_H and F_I are the energy wave number characteristics of the host and impurity atoms respectively, $\vec{r}_v$, $\vec{r}_I$ and $\vec{r}_a$ are the position vectors for vacancy, solute atom and the activated position respectively. Finally $\vec{r}_j^{'} = \vec{r}_j + \vec{\delta}$, $\vec{\delta}$ being the relaxation of n near neighbours having position vectors $\vec{r}_j$ surrounding the activated position of the migrating atom. The total change in migration energy is the sum total of $\Delta E_m^{'}$ and ΔE_R. Temperature dependence of correlation factor C can be determined using either equation (16) or equation (19). For homovalent impurities $(\Delta z = 0)$ it can be assumed that the correlation factor tend to a geometrical constant, independent of temperature and C approaches zero.

10 Different Experimental Methods : Steady State methods

Self and impurity diffusion data have been analyzed in different ways. Many experimental studies on diffusion have been carried out during last few decades [20]. These different techniques are classified in mainly three categories (i) Steady state methods, (ii) Non steady state methods and (iii) Indirect methods.

Steady state methods are based directly on Fick's first law. The usual procedure is to maintain concentrations of the diffusant on the opposite sides of a sample, which is usually a thin sheet or thin walled tube and to measure the resulting steady rate flow. This is generally practicable only when the diffusing element is a gas or can be supplied to and removed from the sample through a vapour phase. There are mainly three ways for the measurements in steady state methods.

(a) Steady concentration distribution within the sample is measured to determine D.

(b) Average gradient calculation from equilibrium data where the surface concentrations c_1 and c_2 in equilibrium with the ambient atmospheres are known and so average D over this concentration gradient can be determined.

(c) Time delay method (measurement of time to reach steady state) is used to determine D. These methods are used for measuring D for interstitial solute diffusion. The Kirkendall effect makes these methods complicated for their reliable application to substitutional diffusion.

11 Non-steady State methods

In non steady state methods the change in concentration distribution in a sample as a result of diffusion is measured and D is calculated from a solution of Fick's second law with proper boundary conditions of the experiment. There are three common types of experimental arrangements two of which are usually employed in chemical diffusion measurements and the third in the measurement of tracer diffusion coefficients.

(a) In diffusion couple method two metals or two different alloys are brought into intimate contact across a plane interface. Diffusion is allowed to take place by annealing at a constants temperature and for a fixed time. The distribution of concentration in the sample is then determined in some convenient manner often by removal and subsequent analysis of a succession of thin layers cut parallel to the initial interface. It is usually arranged such that two halves of the couple are sufficiently thick and the diffusion zone does not extend to either end. D generally varies with concentrations. So, D, can be calculated from concentration (c)- distance (x) curve or from an analytic solution. There are several ways to determine D in this method.

(b) In-diffusion and out-diffusion methods allow the materials to diffuse into or out of an initially homogeneous sample of concentration c_1 under the condition that the concentration at the surface is maintained at a constant and known value c_0 by being exposed to a constant ambient atmosphere. c_1 is usually zero for in-diffusion experiments and c_0 for out-diffusion experiments. Generally three ways are employed in these experiments. D may be calculated from a measurement of either of the total amount of material taken up by or loss from the sample. It may be calculated from the concentration distribution within the sample after diffusion or may be calculated from rate of movement.

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(c) Thin layer methods are used almost exclusively for the measurement of self and tracer D's. A very thin layer of radioactive diffusant of total amount g per unit area is deposited on a plane surface of the sample. After diffusion for time t the concentration at a distance x from the surface is $c(x) = \frac{g}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}}$, provided the layer thickness is very much less that $\sqrt{Dt}$. This condition is easy to satisfy because extremely small quantities suffice for studying the diffusion on account of the very high sensitivity of the methods of detecting and measuring radioactive substances. For the same reason there is a negligible change in the chemical composition of the sample; so D is a constant and Fick's second law can be applicable. Tracer techniques are classified into mainly three categories.

(1) In residual activity method the diffused specimen is subjected to a series of sectioning operations. The layers of thickness x, are removed by lathe sectioning, grinding, etching or anodizing, but the total remaining activity (residual activity), emanating from each newly exposed surface of the sample are measured. A plot of logarithmic activity and x^2 gives the value of D.

(2) In surface decrease method the total activity of the specimen is measured as a function of time. No sectioning is necessary. A plot of activity at $x = 0$ with time yields the value of D.

(3) Serial sectioning method of analysis is most commonly used in the study of diffusion. The diffusion specimen is subjected to a series of sectioning operation after diffusion. To determine the thickness of the material removed, the specimen is weighed before and after each cut. The cuttings are collected and their activity measured with a Geiger-Muller counter or a scintillation counter. A plot of logarithmic count rate versus x^2 yields the slope $\frac{1}{4Dt}$ for volume diffusion and hence D can be calculated if annealing time is known. An alternative auto radiograph method uses a single section cut along or obliquely to the diffusion direction to obtain such a plot. A recent development has been the use of the electron microprobe to measure even impurity diffusion coefficients.

The methods (1) and (2) are generally regarded as less reliable because they obviously also necessitate a knowledge of the absorption characteristics of the radiation concerned. The main advantage of method C is that it is simple, direct and does not depend on the properties of the radiations from the radioactive material used. So it is reliable and accurate method for diffusion analysis.

Table 1

Different indirect methods

Methods	Remarks
1. Internal friction	Stress induced redistribution of atoms is used.
2. NMR study	Diffusional narrowing of resonance lines and atomic mobility to spin lattice relaxation time are used.
3. Magnetic relaxation	Mainly Mossbauer studies.
4. Sintering process	
5. Positron and muon annihilation study	Study of defects, mainly vacancies.
6. Perturbation angular correlation study (PAC)	γ-rays emitted during decay of radioactive atom adjacent to a defect produces a unique change in PAC signal.
7. X-ray or neutron scattering study	Distortions around a defect are studied.

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8. Ion channeling experiment	α - scattering are analyzed by standard pulse height analysis method.
9. Electron microscope observations (both TEM and SEM)	Types of defects, its formation, motion, etc. can be analyzed. Thin film grain boundary diffusion can be studied.
10. Ultrasonic study	Ultrasonic attenuation and velocity measurement as a function of polarization, frequency, temperature and defect density display different types of defects.
11. Resistometric method	Electrical resistance measurement.

12 Indirect methods: A Special case :- Resistometric method

In addition to microscopic diffusion there are a number of other phenomena in solids which depend for their occurrence on the thermally activated motion of atoms and are called indirect methods. From suitable measurements made on some of these phenomena it is possible to determine D. Some advanced techniques can be found in the proceedings of point defects and defect interactions in metals [21]. Table 1 shows all such methods. Here in this paper a brief review of resistometric method will be discussed in the next section.

Among the several experimental techniques employed for studying diffusion in metals as mentioned in the last section the method involving electrical resistivity measurements is one of the oldest. Due to development of direct methods like radioactive tracer technique the resistivity method has been confined only to particular diffusion problems, such as diffusion in semiconductors and diffusion of point defects in quenched, cold worked or irradiated metals. An alternative method of diffusion study using resistometric technique was first suggested by Cerecera where the diffusion equation was solved numerically for the selected experimental conditions in dilute solid solutions of Zn in pure Al [22] and Cu in pure Al [23]. This was found to be useful especially when a stable radioactive tracer of any element is not available. In fact, the reliability and sensitivity of this method has been tested several times viz. for the impurity diffusion of tin in copper and lead in silver [24]; iron in copper within the temperature range of 790°C to 1000°C and nickel in silver within 750°C to 920 °C [25]; nickel in copper and copper–nickel alloys within 780°C to 1037°C [26]; zinc in copper and silver [27]. So it seems worthwhile to review this method. Sen and Ghorai [17] used one of the most complicated members of the simple metal group lead; more so in view of its fast diffusion for several systems. An interstitial configuration of nickel in lead was suggested in a centrifuge study [28]. But it is generally agreed that vacancies play the key role for impurity diffusion in FCC metals. Although diffusion of tin in lead does not fall into fast diffusion category so that it might still be considered as vacancy controlled diffusion; its study itself is of interest because only few measurements of diffusion of tin in lead have been done. The measurements of diffusion of tin in lead by Seith and Laird [29], Decker et. al. [30] and Mei et.al. [31], were all using radioactive tracer technique; so resistometric method is specially useful and interesting in this case.

13 Theory of resistometric method

Let us consider a long circular cylinder in which the diffusion is everywhere radial. The diffusion equation in this condition can be transformed to the one dimensional cylindrical coordinate system as

$$\frac{\partial c}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}(Dr\frac{\partial c}{\partial r}) \qquad (26)$$

Here c is the concentration of diffusing element at time t, r the radial distance from the axis of the cylinder and D the diffusion coefficient. The boundary condition to the problem where a film of diffusing substance is deposited on the surface of the cylinder of radius a and then let to diffuse inside are

A. Case I	At	$t = 0$	$c = \propto$	at	$r = a$
			$= 0$	between	$a > r \geq 0$
B. Case II	Within	$0 < t < \propto$	$c =$ finite	within	$0 \leq r \leq a$
			$\frac{\partial c}{\partial r} = 0$	at	$r = a$
C. Case III	At	$t \to \propto$	$c \to c_f$	within	$0 \leq r \leq a$

These conditions assume that there is no flux of atoms escaping from the surface. Assuming D to be constant for dilute alloys, the solution of equation (26) satisfying the above conditions can be obtained in terms of ordinary Bessel function of the first kind and zero order J_0 as

$$y(x,\tau) = \frac{c(x,\tau)}{c_f} = 1 + \sum_{n=1}^{\propto} \frac{J_0(\alpha_n x) e^{-\alpha_n^2 \tau}}{J_0(\alpha_n)} \qquad (27)$$

Here two dimensionless quantities x and τ are

$$x = \frac{r}{a} \qquad \text{and} \qquad \tau = \frac{Dt}{a^2} \qquad (28)$$

α_n are the positive zeros of the Bessel function of order one such that $J_1(\alpha_n) = 0$.

To connect $y(x,\tau)$ with the change in resistivity data for diffusion the wire can be regarded as consisting of a series of coaxial cylinders having cross section $2\pi r dr$ and the resistivity

$$\rho(r) = \rho_0 + 100\alpha c(r) \qquad (29)$$

Here ρ_0 is the resistivity of the pure base metal, α the increase in resistivity due to 1% of the diffusing element. The total resistance of the wire is given by (case of parallel conductors)

$$\frac{1}{R} = 2\pi \int_0^a \frac{rdr}{\rho_0 + 100\alpha c(r)} = \frac{2\pi a^2}{\rho_0} I(\tau) \qquad (30)$$

Where

$$I(\tau) = \int_0^1 \frac{xdx}{1 + y(x,\tau)} \qquad \text{and} \qquad y = \frac{100\alpha c_f}{\rho_0} \qquad (31)$$

To compare the theory with experimental data it is useful to introduce the normalized function $\phi(t)$ defined as follows

$$\phi(t) = \frac{R_t - R_i}{R_f - R_i} \qquad (32)$$

Here R_i, R_f and R_t are the resistive values of the specimen before, at the end of the diffusion process and after diffusion time t respectively. The corresponding theoretical function $\phi(\tau)$ can be easily calculated from equation (30) as

$$\phi(\tau) = \frac{1}{y}[\frac{1}{2I(\tau)} - 1] \qquad \text{- (33)}$$

Here the relations for R_i, R_f and y are

$$R_i = \frac{\rho_0}{\pi a^2} \qquad R_f = \frac{\rho_0 + 100\alpha c_f}{\pi a^2} \qquad \text{and} \qquad y = \frac{R_f - R_i}{R_i} \qquad (34)$$

The theoretical values of $\phi(\tau)$ for different values of y have already been calculated by Ceresara et. al. [22]. By comparing theoretical $\phi(\tau)$ and experimental $\phi(t)$ at temperature T it is possible to find out the diffusion coefficient D. This procedure is known as isothermal annealing procedure.

There exists another method known as step-annealing procedure, in which y can be determined from comparison of theoretical and experimental ϕ's. The diffusion coefficients at different temperatures can be obtained using equation (28) as

$$\tau_i - \tau_{i-1} = \frac{D_i}{a^2}(t_i - t_{i-1}) \Rightarrow D_i = \frac{a^2(\tau_i - \tau_{i-1})}{t_i - t_{i-1}} = \frac{a^2 \Delta\tau_i}{\theta_i} \tag{35}$$

Where $\Delta\tau_i = \tau_i - \tau_{i-1}$ and $\theta_i = t_i - t_{i-1}$ (36)

θ_i denotes the ith annealing time at temperature T_i. Since choice of origin of time is quite arbitrary this method enables us to measure the diffusion coefficient D_i from equation (35) provided the resistance value before diffusion annealing at temperature T_i is known in order to calculate $\phi(t_{i-1})$ and hence τ_{i-1}. Each of these D_i values obeys Arrhenius law

$$D_i = D_2 e^{-\frac{Q_2}{RT_i}} \tag{37}$$

D_2 is the pre-exponential factor and Q_2 the activation energy for impurity diffusion. T_i's are the different annealing temperatures.

14 Procedure of Resistometric Method

In the experiment a spectral pure metal was drawn in the form of wire with diameter about 10^{-3} m and length about 0.5 m. It was annealed below the two-thirds of the melting point of the metal and then furnace cooled. The surface of the wire was etched to remove any oxide layer following which electroplating procedure was done quickly to avoid oxidation. The initial resistance R_i of the sample mounted inside a cryostat in helium atmosphere and immersed at liquid nitrogen contained in a glass Dewar was determined using Emrick's circuit [32]. After this a series of consecutive short duration thermal treatments were performed and the increase in resistance thereby after each annealing process was measured at liquid nitrogen temperature until a final stable resistance R_f was reached. A dummy resistance was used for any slight variation of liquid nitrogen temperature. In case of diffusion of tin in lead [17] diffusion anneal was performed in the temperature range of $195^\circ C$ to $322^\circ C$ and the value of y was obtained as 0.182 from equation (34) using experimental value of R_i and R_f. Utilizing this value of y a theoretical graph of $\phi(\tau)$ versus τ has been plotted and the corresponding graph has been shown in figure 3. The experimental values of $\phi(t)$ have been determined from equation (32). The corresponding values τ_i have been determined from figure 3. So it is now possible to find the values of D_i, the diffusion coefficient from equation (35). The usual plot of $\log D$ versus T^{-1} obeys Arrhenius law and the values of pre-exponential factor D_2 and activation energy Q_2 have been determined $(D_2 = 0.29\times10^{-4} m^2/s, Q_2 = 1.03 eV)$ and compared with those of some earlier measurements $(D_2 = 0.16\times10^{-4} m^2/s, Q_2 = 0.997 eV)$ [29], $(D_2 = 0.41\times10^{-4} m^2/s, Q_2 = 1.03 eV)$ [30], along with self diffusion values $(D_0 = 0.88\times10^{-4} m^2/s, Q_0 = 1.106 eV)$ [33], $(D_0 = 0.14\times10^{-4} m^2/s, Q_0 = 1.132 eV)$ [34] and $(D_0 = 0.7\times10^{-4} m^2/s, Q_0 = 1.075 eV)$ [35] shown in table 2.

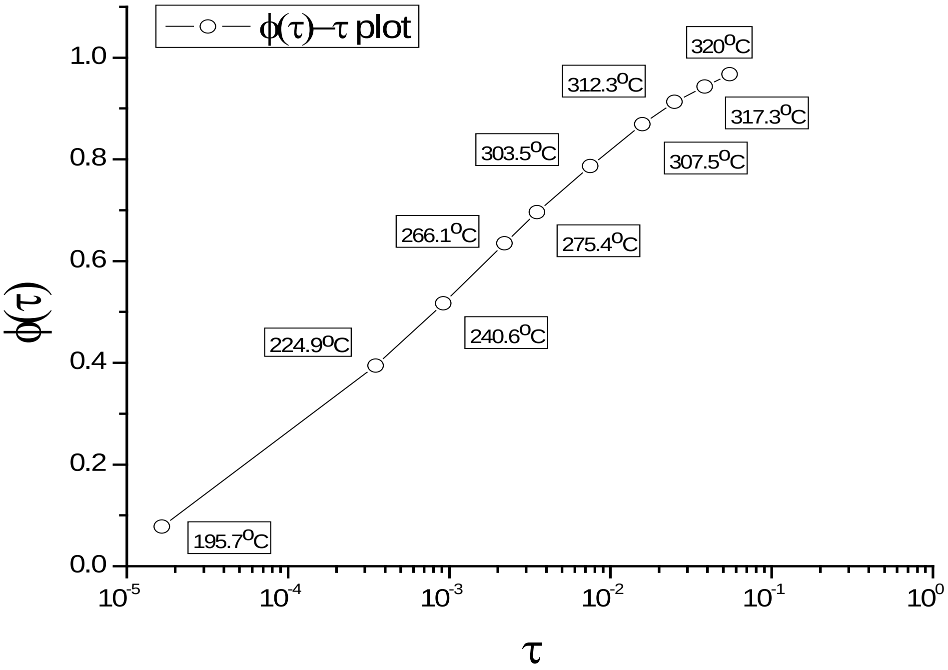

Figure 3 Theoretical plot of $\phi(\tau)$ versus τ for the determination of τ_i corresponding to different temperatures shown in the graph.

Table 2a

Metal	Z^1	a Å^1	T_m °C ^{1}	E_F^{1v} eV	E_M^{1v} eV^3	E_B^{2v} eV	Q_0 eV^7	D$_0$(×10^{-4}m^2/s)^7	E_{coh} eV^1
Cu	1,2	3.61	1083	1.13^3, 1.19^4, 1.28^4	0.95	-0.34	2.186	0.78-0.2	-3.49
Ag	1	4.08	960.8	1.02^3, 1.11^4	0.80	-0.19	1.921	0.67-0.44	-2.95
Au	1,3	4.07	1063	0.90^3, 0.89^4, 0.93^4	0.85	-0.16	1.808	0.091	-3.81
Ca	2	5.57	838	1.10^5		-0.25	1.67	8.3	-1.84
Sr	2	6.05	768						-1.72
γ-Fe	2,3	3.56	1536	1.40^6			2.943	49	-4.28
β-Co	2,3	3.54	1495	1.34^6			2.775	0.23	-4.39
Rh	2,3,4	3.80	1966						-5.75
Ir	2,3,4,6	3.83	2454						-6.94
Ni	2,3	3.52	1453	1.45^3, 1.55^6, 1.79^4, 1.78^4	1.43	0.33	2.914	1.27	-4.44
Pd	2,4	3.88	1552	1.54^3, 1.70^4, 1.85^4			2.758	0.205	-3.89
Pt	2,4	3.92	1769	1.30^3, 1.35^4, 1.32^4	1.37	-0.20	2.952	0.33	-5.84
Al	3	4.04	660	0.66^3	0.64	-0.19	1.474	1.71	-3.39

La	3	5.31	920				1.956	1.5	-4.47
Sc	3	4.53	1539						-3.90
γ-Ce	3,4	5.161	735				1.587	5.5	-4.32
Pr	3,4	5.15	935						-3.37
Yb	3,2	5.47	824						-1.60
Pb	4,2	4.95	327.4	0.50±.03[3], 0.58±.06[3]		-0.23	1.11, 1.13[10]	0.99, 0.7, 0.88	-2.03
Th	4	5.08	1750	1.28±0.23[3]			3.105	395	-6.20
Ne	0		-248.6						
A	0		-189.4						-0.08
Kr	0		-157.3						-0.116
Xe	0		-111.9						-0.16
Rn	0		-71						

[1]Ref. [36], [2]Ref. [20], [3]Ref. [37][38], [4]Ref. [39], [5]Ref. [40], [6]Ref. [41], [7]Ref. [40], [8]Ref. [42], [9]Ref. [43].

Table 2b

Metal	Z[1]	a Å[1]	T_m °C [1]	E_F^{1v} eV	E_M^{1v} eV[3]	E_B^{2v} eV	Q_0 eV[7]	D$_0$(×10^{-4}m^2/s)[7]	E_{coh} eV[1]
Li	1	3.49	453.7	0.48[8]	0.038[8]		0.55, 0.59	0.125, 0.39	1.63
Na	1	4.22	371	0.34[8]	0.03[8]		0.50, 0.44	0.72, 0.15	1.113
K	1	5.22	336.3	0.34[8]	0.038[8]		0.41	0.16	0.934
Rb	1	5.58	312.6				0.41	0.23	0.852
Cs	1	6.04	301.6	0.28[9]					0.804
Ba	2	5.02	1002						1.9
Fe	2	2.87	1811	1.6[6]					4.28
Cr	2	2.88	2133	2.0[8], 2.27[8], 2.08[8]	0.95[8]		3.20, 4.57	1300, 0.2	4.1
Mo	2	3.15	2895	3.0[8], 3.2[8], 3.006[8]	1.35[8]		4.00, 3.48	0.1	6.82
W	2	3.16	3695		1.70[8]		6.64	42.8, 1.90	8.9
V	3	3.03	2202	2.10[8]	0.50[8]		4.58	1280, 0.39	5.31
Nb	3	3.3	2750	2.70[8]	0.55[8]		4.16	1.1	7.57
Ta	3	3.3	3293		0.70[8]		4.28	0.124	8.1
Tl	3	3.87	577				0.87	0.7	1.88
Eu	3	4.58	1091						1.86
Zr	4	3.61	2128				0.85	0.000003	6.25

[1]Ref. [36], [2]Ref. [20], [3]Ref. [37][38], [4]Ref. [39], [5]Ref. [40], [6]Ref. [41], [7]Ref. [42], [8]Ref. [43], [9]Ref. [44].

15 Conclusions

Finally in conclusion, out of several procedures for the determination of properties of self and impurity diffusion [45] only resistometric method has been discussed in details along with three different theoretical models for the bulk samples only and not for thin film samples. Different new mechanisms are observed in thin solid films of metals, bimetallic couples, semiconductors and insulators [46]. The so-called anomalous fast diffusion of metallic solutes has also been observed in a large variety of systems where the atomic size (Wigner-Seitz radius) ratio exceeds the limit of 0.59 and ranging from 0.62 and 0.93 [In fast diffusion impurity or solute diffusivity D_I in several binary systems is several orders of magnitude greater than that of the host or self diffusion D_S of solvent, i.e. $D_I >> D_S$] and Herzig [47] gave one of the earlier reviews on fast diffusion. Hosts here are semiconductors, Gr III and Gr IV metals (Pb, Sn In, Tl), alkali metals (Na, Li), lanthenides and actinides (Pr, U). Noble metals (Cu, Ag, Au), transition or Gr IIB elements (Zn, Cd, Hg) are the fast diffusing impurities. Interstitial mechanism, Interstitisl-vacancy pair mechanism and diplon mechanisms are prescribed for it so far [48].

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