

Review

Point defects in metals

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This review surveys present knowledge of the nature and behaviour of point defects, especially vacancies. The general theoretical concepts and various experimental observations connected with the formation and mobility of vacancies and their complexes, their effect on the physical properties of metals, are described. The formation of secondary defects by vacancy condensation, the interaction between vacancies and solute atoms and some general ideas about point defects, are also discussed in detail.

1. Introduction

Point defects are crystalline irregularities of atomic dimensions. They exist in a crystal at thermal equilibrium while other defects, e.g. dislocations and grain boundaries, are thermodynamically unstable. The existence of point defects in thermal equilibrium was first recognized in the case of ionic crystals in relation to the electrical conductivity inherent in ionic diffusion. It was in about 1950 that the existence of thermal equilibrium vacancies was firmly attributed to metals too, and again in relation to the mechanism for diffusion.

Point defects are important imperfections in crystals because they influence many physical properties of crystalline materials and they are responsible for many diffusion controlled processes. The mechanical properties of metals are also sensitive to the presence of point defects because of their interactions with dislocations. Diffusion processes, which often govern many solid state reactions, are largely controlled by the migration of point defects, primarily vacancies.

In this review a description of the nature and behaviour of point defects is given. This includes the presence of vacancies in thermal equilibrium, lattice distortions around point defects, formation energy of a vacancy, binding energy between vacancies in thermal equilibrium, lattice distortions around point defects, formation energy of a vacancy, binding energy between vacancies, mobility of point defects, the methods of production of point defects, their effect on the properties of

metals, and their role in diffusion processes. We shall also summarize some theories of point defects and impurities or other defects.

It is impossible in the space available to survey all the important fields connected with the subject. Our discussion is limited, therefore, to areas which we felt to be of most basic significance and to some selected problems which serve as examples of more general phenomena connected with point defects. Such a selection is, of course, somewhat arbitrary, and reflects to some extent the authors' own interest. Some topics are mentioned only briefly and rather qualitatively but references are given to the more important papers. Inevitably, some important aspects are omitted, such as the role of vacancies on high temperature mechanical properties, the investigation of vacancies by positron annihilation and so on.

2. Point defects due to thermal equilibrium

The free enthalpy, G , of a crystal (given by $G = H - TS$ at temperature T , where H is the enthalpy of the crystal and S is the entropy) changes on the introduction of point defects. This occurs in three ways: (1) by the internal energy of their formation energy, E_F , (2) by the entropy of formation, S_F , and (3) by the configurational entropy of the crystal, S_C . The entropy change, S_F , arises mainly from the change in the vibrational frequency of the atoms surrounding the point defect.

In order to calculate the thermal equilibrium

vacancy concentration, C_0^V , an elementary treatment is applied [1] which leads to the expression

$$C_0^V = \exp\left(\frac{S_F^V}{k}\right) \cdot \exp\left(-\frac{H_F^V}{kT}\right) \quad (1)$$

The concentration of interstitials in thermal equilibrium, C_0^I , is derived in a similar way:

$$C_0^I = q \exp\left(\frac{S_F^I}{k}\right) \cdot \exp\left(-\frac{H_F^I}{kT}\right) \quad (2)$$

Here, S_F^I and H_F^I refer to interstitial atoms and q is the number of interstitial sites in each normal lattice site.

In any crystal, only those point defects which do not disturb the electrical equilibrium of the crystal can be formed, i.e. the crystal remains outwardly neutral. For metals this condition does not mean any restriction, since a neutral atom is removed or inserted. With ionic crystals the situation is quite different. If, for instance, a vacancy were formed by the removal of a negative ion, the electrical equilibrium would be upset. Consequently, in an ionic crystal, positive and negative vacancies are always formed simultaneously (Schottky defects). Another possibility is the formation of a vacancy – interstitial pair of the same type (Frenkel defect). If the crystal contains impurities whose ions have an electrical charge different from that of the base material, the vacancy concentration (i.e. the number of vacancies created at positive and negative lattice sites) may deviate from that of the pure crystal.

As seen from Equations 1 and 2, the concentrations of point defects at temperature T is mainly determined by their formation energies. According to theoretical calculations, H_F^I in fcc metals is a few times larger than H_F^V , and hence most of the point defects in thermal equilibrium are expected to be vacancies. The same is also generally true for bcc and hcp metals. This is seen by taking E_F^I to be 2 eV and E_F^V to be 1 eV. The ratio C_0^I/C_0^V is then about 10^{-5} at 1000 K with $S_F^V = S_F^I$ and $q = 1$. This prediction has been confirmed by experiments. Therefore, the point defects in thermal equilibrium are predominantly vacancies, and so we shall confine our discussion to them.

3. Formation energy of a vacancy

The most important factor determining the equilibrium concentration of vacancies is the forma-

tion enthalpy, H_F^V . In the following, a short review of the theoretical and the experimental results for H_F^V is given.

3.1. Theoretical

In most of the theoretical calculations, the following procedure has been applied: an atom is removed from a normal lattice site inside a crystal, leaving behind a vacant lattice site, and is placed on the surface (Fig. 1). Therefore, the volume of the crystal increases while the surface area is substantially unaltered. Relaxation of the lattice and redistribution of electrons around the vacancy must be taken into account.

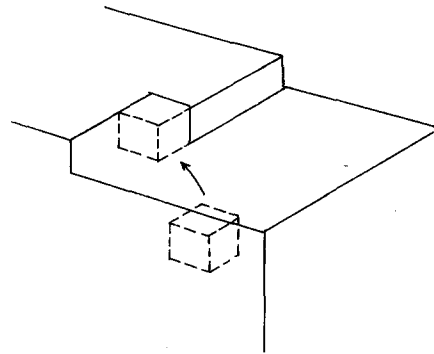


Figure 1 Process of formation of a vacancy.

3.1.1. Calculation methods for H_F^V using macroscopic concepts

Brooks [2] calculated the change of internal energy, E_F^V , in the following way: upon creating a vacancy, a spherical surface of radius r_s is formed inside the crystal. This surface contributes to the surface energy proportional to r_s^2 . The vacancy will tend to decrease in size and, therefore, decrease the surface energy by distorting the surrounding material. This relaxation causes an increase in the elastic energy proportional to $r_s^3 \epsilon^2$ (ϵr_s is the displacement of the surface). The sum of the surface energy and the elastic energy has a minimum at a particular value of ϵ ; this minimum value is considered to be the formation energy. Brook's result gives about 1.8 eV for a vacancy in copper. The formation energy of an interstitial atom was also estimated in the same manner and found to be about 9 eV in copper. This method is only a rough approximation, in that it uses macroscopic concepts, e.g. surface energy and linear elasticity.

3.1.2. Calculation E_V^Y using quantum mechanics

All calculations were based upon the free electron model with a hard ion core. The formation of a vacancy in a crystal is assumed to increase the volume of a box containing free electrons, with a corresponding decrease in the electronic energy. At the position of the vacancy, the potential energy for electrons differs from that of the others. The perturbing potential causes an increase in the kinetic energy of the electron. These changes were calculated using the variational method [3], and the self consistent method [4] for copper. The perturbing potential was taken to be equal to the negative of the potential due to a copper ion. This calculation uses essentially the same method as that applied by Fuchs [5–7] for the cohesive energy of copper, and hence includes all other effects contributing to the electronic energy, such as the Coulomb and the exchange energy. Fumi considered a vacancy as an impurity atom of -1 valency [8] and calculated the change in the kinetic energy using Friedel's sum rule [9] to estimate the number of electrons disturbed by the vacancy. However, Fumi's calculation does not include the changes in the Coulomb energy and in the exchange energy, as pointed out by Lomer [10].

Besides the electronic energy discussed so far, one must also consider the energy due to ion interaction. Two neighbouring ions repel each other. This is a closed shell repulsion and is due mainly to the exchange interaction between the electrons in the different closed shells. The energy due to this effect is usually represented by a Born–Mayer potential of the form

$$D \exp \left\{ -\frac{\alpha(r-r_0)}{r_0} \right\},$$

where r_0 is the equilibrium nearest-neighbour separation distance. The parameters D and α are determined empirically by comparing the elastic constants calculated from this potential with the experimentally determined values. When a vacancy is formed, the atoms surrounding it move inward and the distance between the ions increases, causing a decrease in the repulsive potential energy. In the case of copper, this energy decrease amounts to about 0.3 eV. The formation energy of a vacancy resulting from this calculation, from electronic and ionic energy considerations, turns out to be about

1.2 eV. A calculation made by Seeger and Mann [11] gives results.

Thus, the various values calculated for the formation energy of a vacancy in copper lie between 0.91 and 1.45 eV. It should be noted that the predominant term determining the formation energy of a vacancy is the change of the electronic energy. However, for an interstitial atom, the ion pair potential is predominant in determining the formation energy. This may be true for other "full" metals, where the nearest neighbour distance is almost equal to the ion diameter.

A rigorous quantum mechanical calculation for metals other than monovalent ones has not yet been made. Nevertheless, Johnson [12], assuming an interatomic potential including repulsion and attraction, has programmed a calculation for the formation energy of a vacancy in γ -iron and in nickel, that yields results of about 1.5 eV.

3.2. Experimental methods

The formation energy of a vacancy has been determined fairly accurately by various experimental methods. The experimental techniques are divided into two groups: techniques to determine the concentration of thermal equilibrium vacancies at high temperatures, and quenching high-temperature thermal equilibrium concentrations to low temperatures, where the concentrations may be determined by appropriate measurements. The concentrations of vacancies are normally determined by measuring the change of some physical property which is considered to be a monotonic function of the concentration. However, most physical properties depend both on the presence of vacancies, and on temperature. Therefore, it is of critical importance in the determination of vacancy concentrations to differentiate the effect of temperature from the effect of vacancies on the physical property being measured. The simplest way to do this is to measure the property at a constant temperature low enough to suppress the temperature effect as much as possible. For example, the electrical resistivity depends linearly on the concentration of vacancies if aggregation of vacancies is negligible. At low temperatures, the thermal component of resistivity is small and the effect of vacancies may be large enough to be measured accurately. At these low temperatures, however, the equilibrium concentration is too small to be detected. If, on the other hand, the equilibrium concentration of the vacancies at a high temperature can be quenched

into the metal, it can then be determined at a low temperature by measuring the electrical resistivity. This technique is one of the most powerful methods for determining the equilibrium concentration of vacancies and hence their "formation energy".

A disadvantage in the quenching method is the possible aggregation or annihilation of some of the vacancies during quenching. It is then more desirable to determine the equilibrium concentration at a high temperature. One can define equilibrium studies of point defects as investigations in which the point defect concentrations are either equal or very close to the concentrations of thermal equilibrium. The experimental investigations of point defects in such a case need *in situ* measurement of the chosen property and may be divided into three classes:

(1) determination of the nature and quantitative measurement of the concentration of point defects in thermal equilibrium. For metals some of these techniques are (a) the measurement of the electrical resistivity, specific heat or thermal expansion and their variation with temperature; (b) the comparison of the relative change of specimen length $\Delta l/l_0$ and of the relative change of lattice parameter, $\Delta a/a_0$; (c) the measurement of the γ radiation resulting from the annihilation of positrons trapped at vacancies.

(2) Measurement of tracer diffusion, in particular of self diffusion and of the transport of matter, e.g. thermo- or electrotransport. These measurements give information on the diffusion coefficients and on the diffusion mechanism of point defects.

(3) Resonance and relaxation experiments which are capable of giving information on the jump frequencies of nuclei and on self diffusion mechanisms.

Separation of the effect of the thermal component of the properties studied from the vacancy contribution is the most critical part of the *in situ* methods. If a single property is measured as a function of temperature, the separation can be made as follows: the temperature dependence of the property is measured at a low enough temperature for the effect of thermal vacancies to be negligible, and is extrapolated to the high temperature. Another method is to calculate the thermal component at high temperatures. The thermal component so determined is subtracted from the measured values. Both these estimates of the high temperature thermal component do not, however,

always turn out to be valid.

Electrical resistivity, specific heat and thermal expansion measurements have been widely applied to determine the vacancy formation energy. This is, in fact, the activation enthalpy but for normal pressures, the term $p\Delta V$ can be neglected, and so the two are identical. For complete reviews and references concerning the equilibrium investigations of point defects, we refer to the articles by Seeger and Mehrer [13], Seeger [14], Kraftmakher and Strelkov [15], [16] and Hoch [17].

It is of historical interest to note that Meechan and Eggleston [18] were the first to measure the resistivity of copper and of gold as a function of temperature to determine the effects of vacancies. They fitted the data below 500° C to an equation of the type

$$R = a + bT + cT^2.$$

The logarithm of the extra resistivity over that due to the extrapolated curve of this equation above 600° C was plotted against the reciprocal of the absolute temperature. A straight line was obtained and the formation energy was calculated to be 0.9 ± 0.5 eV in copper and 0.67 ± 0.07 eV in gold. With the calculated resistivity per at. % vacancies and the observed extra resistivity, they estimated the concentration of thermal vacancies at or near the melting point to be of the order of 10^{-2} . The formation energies so determined are found to be close to the theoretical values. The estimated concentrations, however, are too large. For example, if we accept $E_F^V = 0.9$ eV, then Equation 1 gives a concentration of about $5 \times 10^{-4} \exp(S_F^V/k)$. In order to obtain a concentration of the order of 10^{-2} , the exponential factor would have to be larger than 20, but most investigators consider this to be too large. Moreover, Nicholas [19] pointed out other possibilities for explaining the observed extra resistivity without introducing vacancies.

In order to determine the equilibrium concentrations of vacancies by measuring a property as a function of temperature, the thermal component of the property must be determined unambiguously. A simultaneous determination of the lattice parameter and thermal expansion is the only technique so far reported to establish this point. The expansion of a specimen is caused by both the thermal dilatation of the lattice due to the change of temperature and the presence of vacancies, which results in an increase in the number of lattice sites

together with the lattice relaxation around vacancies. The X-ray determination of the lattice parameter detects only the thermal expansion and the relaxation around vacancies but not the presence of vacant sites. Therefore, taking the difference between the fractional change in the lattice parameter and in length, one may obtain the number of vacant lattice sites. There is little uncertainty in considering that thermal expansion of the

lattice causes the same fractional change in length and lattice parameter. Eshelby [20] showed that randomly distributed centres of dilatation cause the same effect on length and the X-ray measured lattice parameter. Accordingly, Balluffi and Simmons [21] applied the Eshelby treatment to centres of dilatation of a non-elastic nature, e.g. vacancies. Hence, the increase in the atomic sites $\Delta N/N$ is given by

TABLE I Entropy and energy of formation of a vacancy in pure metals (According to Kimura and Maddin [35]).

Metal	Formation entropy S_F/k	Formation energy E_F (eV)	Method*	Reference
Au	—	0.79	R	Lazarev and Ovcharenko [36]
	—	0.95	R	Bradshaw and Pearson [37]
	—	0.98	R, L	Bauerle and Koehler [38]
	—	0.98	RS	Takamura <i>et al.</i> [39]
	—	0.97	RR	Mori <i>et al.</i> [40]
	—	0.96	R	Jeannotte and Macklin [41]
	—	0.97	C	de Sorbo [42]
	—	0.98	LS	Takamura [43]
	1.0	0.94	EQ	Simmons and Balluffi [29]
Al	—	0.76	R	Bradshaw and Pearson [44]
	—	0.76	R	Panseri and Federighi [45]
	—	0.79	R	de Sorbo and Turnbull [46]
	—	0.79	R	de Sorbo [47]
	—	0.76	RS	Okazaki and Takamura [48]
	—	0.75	R, L	Detert and Stander [49]
	—	0.73	RR	Bass [50]
	2.4	0.76	EQ	Simmons and Balluffi [51]
Ag	—	1.01	C	Gertsriken and Novikov [52]
	—	1.06	R	Quere [53, 54]
	—	1.10	R	Doyama and Koehler [55, 56]
	1.5	1.09	EQ	Simmons and Balluffi [27]
Cu	—	1.00	R	Airoldi <i>et al.</i> [57]
	—	1.06	R	Hasiguti <i>et al.</i> [58]
	—	1.14	R	Wright and Evans [59]
	1.5	1.17	EQ	Simmons and Balluffi [28]
Pt	—	1.4	R	Bradshaw and Pearson [60]
	—	1.18	R	Lazarev and Ovcharenko [36]
	—	1.23	R	Ascoli <i>et al.</i> [61]
	—	1.20	R	Baccella <i>et al.</i> [62]
	—	1.51	R	Jackson [63]
W	—	3.32	R	Schultz [64, 65]
Pb	0.7	0.49	EQ	Feder and Nowick [31]
Mg	—	0.89	R	Beevers [66]
Sn	—	0.51	R	de Sorbo [67]

* C, calorimetric measurements.

LS, length change measurement with specimen size correction.

R, resistivity measurement.

RS, resistivity measurement with specimen size correction.

RR, resistivity measurement with quenching rate correction.

EQ, length and lattice parameter measurement at thermal equilibrium.

$$\frac{\Delta N}{N} = 3 \left(\frac{\Delta L}{L} - \frac{\Delta a}{a} \right),$$

where L is the length and a the lattice parameter. If the point defects formed are interstitial atoms, $(\Delta L/L) - (\Delta a/a)$ is negative. In none of the metals so far investigated in equilibrium has this sign been found to be negative. This fact shows clearly that in equilibrium C^I is negligible compared to C^V . An important feature of the above expression is that it gives the change in the number of atomic sites regardless of the amount of lattice relaxation around the defect.

Measurements of this type published in the literature were done on Al [22–26], Ag [27], Cu [28], Au [29], Pb [30, 31], Na [32, 33] and Cd [34]. Some of the results obtained are given in Table I.

Another important method which is suitable for measuring the equilibrium concentration of vacancies due to high temperatures is the quenching method, if the loss of vacancies (together with any possible production of them, e.g. by quenching strains) during quenching can be avoided or accurately corrected. A correction is possible by changing the specimen size or quenching rate. A detailed discussion of the vacancies produced by quenching will be given in the chapter dealing with the production of point defects, but the values determined by the quenching method are also given in Table I. The vacancy concentrations after quenching are determined usually by measuring the extra resistivity. In general, even when quenching from high temperatures by a high quenching rate, there is still vacancy aggregation to some extent, and this affects the property being measured. In calculating the formation energy, it is assumed, however, that association is negligibly small or that the property being measured is not changed by the association (i.e. the same contribution arises from two isolated vacancies as from a divacancy). Since fair agreement exists between the values obtained by the equilibrium methods (not affected by the association) and those obtained by the quenching method (corrected for associations of vacancies during quenching), the effect of associations may not be very appreciable at high temperatures. Associations, however, become quite important at low temperatures if excess concentrations of vacancies due to high temperature thermal equilibrium are frozen-in.

4. Lattice distortion around point defects

If a metal ion in a crystal is removed from the interior and is placed on the surface of the crystal creating simply a new substitutional atom site without any relaxation, the crystal expands by one atomic volume. In practice, however, the net volume expansion due to the introduction of a vacancy into a crystal is less than one atomic volume because of the lattice distortion arising from the displacement of the surrounding atoms from their equilibrium positions, so that the total free energy of the crystal is minimized.

According to Eshelby [20, 68], the volume change ΔV on introducing a centre of dilatation, of strength C , into a homogeneous isotropic elastic body with a stress-free surface is given by

$$\Delta V = 4\pi\gamma C, \quad (3)$$

with $\gamma = 3(1 - \nu)/(1 + \nu)$, where ν is the Poisson's ratio and γ a constant, about 1.5 for most metals. For vacancies in an infinite medium Equation 3 is valid. With use of this equation the change of volume of a body containing a vacancy can be determined taking into consideration the diffusion of an atom to the surface whenever a vacancy is created [69]. If no other change took place in the lattice, every vacancy would increase the volume of the body as we mentioned before by one atomic volume. However, because of the image displacement, the volume of the crystal decreases by [69]:

$$\Delta V_i = (\gamma - 1)\Omega.$$

where Ω is the atomic volume. The resultant change of volume in a body containing a single vacancy is consequently

$$\begin{aligned} \Delta V &= \Omega - (\gamma - 1)\Omega \\ &= \left(\frac{5\nu - 1}{\nu + 1} \right) \Omega. \end{aligned}$$

Taking $\nu = \frac{1}{3}$ one obtains $\Delta V = 0.5\Omega$, which is in very good agreement with the values obtained for gold experimentally $(0.57 \pm 0.05)\Omega$ [55], and $(0.45 \pm 0.1)\Omega$ [28]. In this approximation of an isotropic elastic continuum where the atomic structure is smeared out, the elastic displacement caused by a centre of dilatation in a finite crystal is given in a spherically symmetric form as $u = Cr/r^3 + Br$. Here B is a constant expressed by $B = 2C(1 - 2\nu)/R^3(1 + \nu)$ for a spherical body with a radius R .

As a first approximation, such continuum theory may give useful information about the lattice distortion, but the actual displacement of atoms in the vicinity of a defect may not be in such a simple form.

The interaction of atoms in metals roughly consists of two contributions, one is from ion-core repulsion and the other is from valency electrons. For noble metals and transition metals such as iron, cobalt and nickel the contribution from the ion-core repulsion is more important, while the electric contribution is dominant for alkali metals and some non-transition metals such as zinc and aluminium. However, it is difficult for any metals to describe these contributions separately in the explicit form. For convenience, suitable two-body interaction potentials have been used for the calculations. The typical potentials frequently used so far are the Born-Mayer, Morse and composite cubic types.

In the usual method for the calculation of atomic displacements around a point defect, the crystal is divided into three regions, i.e. region I around the defect, a boundary region II around region I, and the outermost region III. In region I, atoms are allowed to interact with surrounding atoms according to the pair-wise interaction force assumed. Atoms in regions II and III are treated as discrete particles embedded in elastic continuum, but atoms in region III do not interact with those in region I. When the assumed potential gives only repulsive forces as in the case of the Born-Mayer potential, it is necessary to stabilize the model crystal by an appropriate method. The most stable configuration around the defect can be obtained by minimizing the crystal energy with reference to the displacement of each atom.

Calculations show that the nearest neighbours around a vacancy are relaxed inwards for noble metals and several transition metals, while in metals, such as aluminium they are relaxed outwards. The nature of the atom displacement around a vacancy can be more easily understood from the oscillating pair-wise interaction potential derived from the pseudo-potential theory (see for example, Harrison [70]; Torrens and Gerl [71]).

5. Binding energy between vacancies

In 1952 Seitz [72] suggested that the energy of association of a pair of vacancies in copper may be large, leading to formation of divacancies which are very mobile. The first estimate for the binding

energy of a divacancy E_{2V}^B was due to Bartlett and Dienes [73] who considered the binding energy between two atoms to be approximately 1/6 of the cohesive energy, and thus estimated E_{2V}^B to be about 0.5 eV for copper. Weizer and Girifalco [74] calculated the binding energy of a divacancy in copper using a Morse potential function and they determined its value to be 0.64 eV. They also found that two vacancies attract each other if the vacancies are less than 7 Å apart but they do not interact appreciably at separations greater than 7 Å. More rigorous quantum mechanical calculations have been performed by Seeger and Bross [75], resulting in a value of about 0.3 eV for noble metals.

A number of investigators have employed computers to calculate the defect energies. Assuming interatomic potentials, the energy of a crystal containing several hundreds to several thousands of atoms is calculated as a function of atomic configuration around a defect. The minimum energy obtained is the defect energy. It is naturally expected that the calculated value depends on the form of the assumed interatomic potential. The effect of redistribution of electrons is not taken into account. Hence, at present, the absolute value of the defect energy may be taken as reliable.

The concentration of divacancies C_{2V} present in equilibrium with single vacancies with a concentration C_{1V} for fcc metals can be given as [76]:

$$C_{2V} = 6 C_{1V}^2 \exp \left\{ \frac{E_B^{2V}}{kT} \right\}, \quad (4)$$

with $E_B^{2V} = 2E_F - E_F^{2V}$ where E_F^{2V} is the formation energy of a divacancy.

This is derived by equating the rate of formation of divacancies to the rate of their decomposition. The formation rate is

$$\frac{dC_{2V}}{dt} = 84 C_{1V}^2 \nu_1 \cdot \exp \left\{ -\frac{E_M^V}{kT} \right\},$$

where E_M^V is the activation energy for migration of a vacancy and ν_1 the atomic vibration frequency around a single vacancy. The factor 84 is the number of effective atomic sites from which a vacancy jumps into one of the nearest neighbour sites to form a divacancy. This is the product of the number of nearest neighbour sites of one vacancy (= 12) and the number of non-common neighbours (= 7) for each of these 12 sites. The rate of de-

composition is:

$$-\frac{dC_{2V}}{dt} = 14\nu_2 C_{2V} \exp\left\{-\frac{E_M^V + E_B^{2V}}{kT}\right\}.$$

The factor 14 is the number of ways a divacancy can dissociate. Each vacancy can move into seven sites which are not the common nearest neighbours of the other vacancy. It is assumed that $\nu_1 = \nu_2$ and that the interaction between vacancies ranges only to the nearest neighbour atomic sites. Equation 4 holds for non-equilibrium concentrations of vacancies if the total number of vacant lattice sites remains constant or changes very slowly, compared with the rate of establishing single vacancy-divacancy equilibrium. Because gold is widely investigated we shall take it as an example. In

TABLE II Ratio of divacancy concentration to single vacancy concentration at various temperatures, and binding energies, E_B^{2V} (E_F^{1V} is taken to be 1.0 eV). After Kimura and Maddin [35]

Binding energy E_B^{2V} (eV)	C_{2V}/C_{1V}			
	300 K	500 K	1000 K	1200 K
0.1	8×10^{-14}	4×10^{-8}	8×10^{-4}	4×10^{-3}
0.2	3.2×10^{-12}	4×10^{-7}	2.5×10^{-7}	1×10^{-2}
0.3	1.6×10^{-10}	4×10^{-6}	4×10^{-6}	2.9×10^{-2}

Table II the ratio C_{2V}/C_{1V} for gold at various temperatures with C_{1V} at thermal equilibrium, is shown. The binding energy E_B^{2V} is assumed to be 0.1, 0.2 and 0.3 eV. Even for the largest value assumed (0.3 eV), the number of divancies is, at most, about 2% of the single vacancies. If quenching is ideal, i.e. no divancies are formed during quenching, the quenched-in resistivity consists of the resistivity due to single vacancies (96% of the vacant sites) and of that due to divancies (4% of the vacant sites). If the resistivity decrease is $\Delta\rho$ by the formation of a divacancy, the fractional difference between the total resistivity due to N single vacancies and that due to 98% single vacancies and 2% divancies is $0.04 \Delta\rho/\rho$. This ratio is not known, but may be assumed to be about 0.1. Thus we may have about 0.4% difference between resistivities with and without vacancy association at the melting point. Below 800°C , however, the difference is about 0.1%. Since the formation energy is usually determined by quenching from below 850°C in gold, vacancy aggregation affects the calculated value of the

formation energy only very slightly.

Experimental determinations of the binding energy have not yet been made. Somewhat indirect estimates, however, have been made by several investigators. Since the mobility of divancies in fcc metals is considered to be much larger than that of single vacancies, a careful investigation of the decay rate of excess vacancies may provide information about the concentration of divancies. The activation energy for the migration of single vacancies can be calculated as the difference between the activation energy for self-diffusion and the formation energy of vacancies. If the observed activation energy for excess vacancy decay is smaller than the migration energy of single vacancies, the difference is attributed to the existence of divancies. Thus the binding energy is estimated, assuming the equilibrium between the concentration of single and divancies and a value for the activation energy for divacancy migration, to be between 0.1 and 0.3 eV in gold (e.g. [13, 77–82]). It should be noted that the decay of excess vacancies strongly depends on the purity of the specimen and a technique is required to detect directly the existence of divancies and so an accurate determination of the binding energy is not yet possible.

No experiments have been attempted to determine the binding energies of clusters containing more than three vacancies. This is an even more difficult problem than determining the divacancy binding energy.

6. Mobility of point defects

6.1. Mobility of single vacancies

Vacancies and interstitials in a solid are mobile at a sufficiently high temperature since, to change its position, a defect has to surmount a potential barrier. This process is usually treated on the basis of absolute reaction rate theory [83], although some attempts have been made recently at a dynamic approach [84]. For a detailed discussion about this problem we refer to both the work of Damask and Dienes [85] and Peterson [86] in which the frequency, ν , of a vacancy jump is given by

$$\nu = BZ\nu_0 \cdot \exp\left\{-\frac{E_M^V}{kT}\right\} \quad (5)$$

with $B = \exp(S_M^V/k)$, where S_M^V is the activation entropy for the vacancy migration, Z is the coordination number, ν_0 the atomic vibration fre-

quency and E_M^V the activation energy for migration of a vacancy. This equation, based upon thermal equilibrium between the normal state and the activated state, may be applied to the migration of excess vacancies, e.g. to an arrangement when a crystal is not in thermal equilibrium. A consideration of the migration of vacancies is important because of its role in self-diffusion in metals. At this stage a connection can be made with the diffusion in solids. The probability of atomic migration (the rate of self-diffusion) is proportional to the probability of finding a vacancy next to an atom (the vacancy concentration C_V) and to the frequency of an atomic jump into the vacancy position ν/Z . Hence, for the self-diffusion coefficient D we have

$$D \sim C_V \frac{\nu}{Z}.$$

If diffusion takes place under thermal equilibrium conditions (a condition for "normal" diffusion),

$$D \sim \exp \left\{ -\frac{E_F^V + E_M^V}{kT} \right\}.$$

Hence, the activation energy for self-diffusion E_D is

$$E_D = E_F^V + E_M^V. \quad (6)$$

If diffusion is caused primarily by excess vacancies the apparent activation energy for self diffusion is E_M^V . Diffusion enhanced by excess vacancies happens also in low temperature ageing of quenched supersaturated solid solutions.

Quantum mechanics calculations of the migration energy have been made together with calculations of the formation energy of a vacancy in order to understand the mechanisms of self-diffusion. The calculations, however, are less reliable than those for the formation energy. This is so because the migration energy is considered to be the difference between the energy of a vacancy in the normal site and that in the saddle point configuration, both of which are calculated with fairly large inaccuracies.

TABLE III Activation energy for self-diffusion, E_D (experimental), formation energy of a vacancy, E_F^V (experimental), and the calculated migration energy $E_M^V (= E_D - E_F^V)$ in some fcc metals

Metal	E_D (eV)	E_F^V (eV)	$E_M^V (= E_D - E_F^V)$ (eV)	Reference for E_D
Au	1.84	0.96	0.88	Gilder and Lazarus [87]
Ag	1.92	1.09	0.83	Tomizuka and Sonder [88]
Cu	2.05	1.1	0.95	Kuper <i>et al.</i> [89]
Al	1.48	0.76	0.72	Lundy and Murdock [90]

The activation energy for migration of a single vacancy can be determined experimentally from the temperature dependence of their decay, if only single vacancies exist in excess. As will be described later, excess vacancies can be produced in a metal by various methods. Except for the quenching method, however, other defects, e.g. interstitial atoms and dislocations, are also produced. The physical properties suitable for detecting vacancies are usually affected by these defects as well, and hence it is difficult to attribute to vacancy decay, without ambiguity, any change in a physical property during annealing. Moreover, the process of vacancy decay may be affected by the existence of other defects, even when divacancy formation does not occur.

Many investigations have been carried out to determine the activation energy of vacancy migration in quenched metals. However, a dependably accurate determination has not been made because of two reasons: (1) the formation of the more mobile divacancies, and (2) the effect of impurity atoms. In noble metals single vacancies move with an activation energy between 0.6 and 1 eV.

A reliable method for estimating the migration activation energy of single vacancies, particularly in aluminium, is to subtract the determined formation energy, E_F^V , from the determined self-diffusion energy, E_D . With radioactive tracer techniques, the activation energy for self-diffusion, E_D , can be determined fairly accurately, and the formation energy of a vacancy, E_F^V , can also be determined fairly accurately from equilibrium or from quenching methods. The relationship between E_D , E_F^V and E_M^V is well established and the resulting values shown in Table III, are fairly reliable, if the effect of divacancies on self-diffusion is small.

6.2. Mobility of divacancies

Divacancies are more mobile than single vacancies, i.e. the divacancy migration activation energy is smaller than that of a single vacancy. The explanation is given by studying the mechanism of the divacancy motion. When a divacancy moves, then

one atom, the common nearest neighbour atom of the two vacancies, jumps into one of the vacant sites. The resistance to the atomic jump comes mainly from the closed shell repulsion between ion cores. The lattice around a divacancy is more relaxed than around a single vacancy. Moreover, for a divacancy the lattice has more tolerance for local atomic displacements than for a single vacancy.

Rigorous calculations of the activation energy are difficult and experiments have not yet been made to provide a check. However, we may consider the divacancy migration energy in noble metals to be 0.2 to 0.3 eV, smaller than that for a single vacancy. The situation may be somewhat different in bcc metals, where a divacancy may take a second-nearest neighbour configuration in making one jump. Also, the atomic bond character is partly directional.

6.3. Mobility of vacancy clusters

Clusters of more than three vacancies may migrate, but with a mobility smaller than that for single vacancies or divacancies. If we consider trivacancies as an example, de Jong and Koehler [79] and

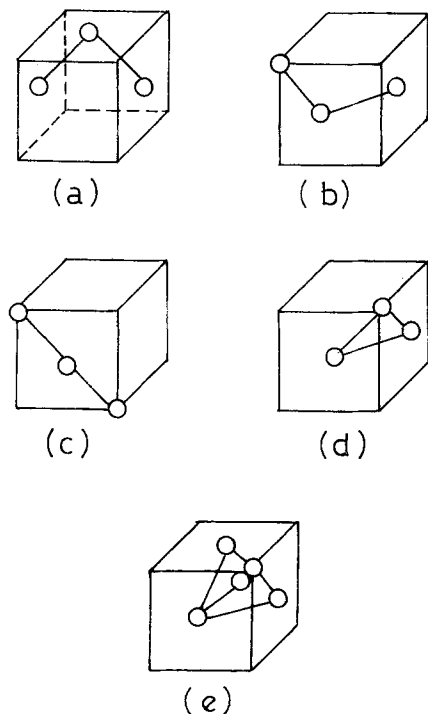


Figure 2 Five configurations of a trivacancy. (After Doyama and Cotterill [91]). (a) 90° , 0.75 eV; (b) 120° , 1.20 eV; (c) 180° , 1.13 eV; (d) 60° ; (e) tetrahedron. The energies are relative to configuration (d).

Doyama and Cotterill [91] classified them in to five possible configurations (Fig. 2). The most compact trivacancy has the configuration that three vacancies lie on a (111) plane forming an equilateral triangle (Fig. 2d). The atom which is the common nearest neighbour of the three vacancies probably moves to the centre of the tetrahedron [100] (Fig. 2e). The other configurations are not compact and have only two bonds between vacancies. If a trivacancy possesses the configuration shown in Fig. 2d or e, it cannot migrate without changing its configuration. At first glance, configuration (d) appears to be mobile, but careful consideration shows that it merely oscillates since only one atom can jump into one of the three vacant sites and thus the atom simply moves back and forth between the original position and one of the three vacant sites. In order to move a trivacancy of configuration (d), it must first take the configuration shown in (a) or (b). A possible sequence of configurational changes for trivacancy migration is shown in Fig. 3. The mobility is determined by the step with the highest activation energy. The first step, i.e. breaking the configuration (d), probably requires the highest activation energy, because an additional energy to break the configuration must be added to the activation energy for the atomic jump. As described above,

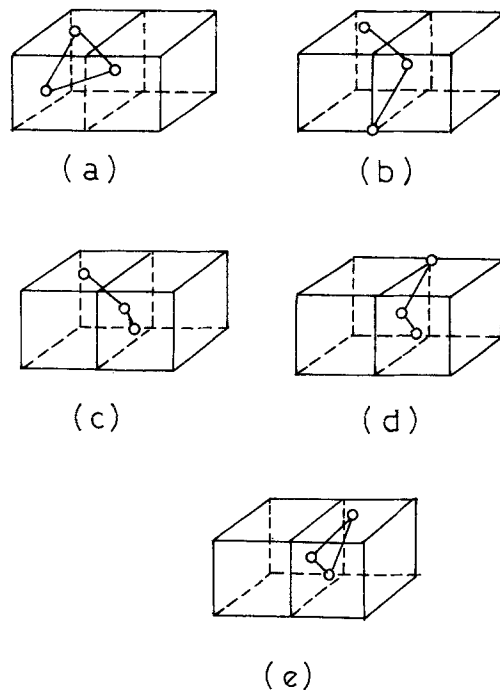


Figure 3 An example of a trivacancy migration sequence.

the energy of configuration (d) is smaller than that of configuration (a) or (b). The activation energy for an atomic jump may be somewhat smaller than that for a divacancy since in the latter case there is more lattice relaxation.

Considering these two effects, one may take the trivacancy migration energy (configuration d) to be about the same as for a single vacancy. Since more than two steps are involved in one unit jump of a trivacancy, the net mobility of a trivacancy would be smaller than that for a single vacancy. However, a trivacancy of configuration (e) may be less mobile than that of configuration (d), because configuration (e) is considered to have a smaller energy than configuration (d). As the temperature is lowered, a trivacancy tends to transform to configurations of smaller energy. Hence, at low temperatures, e.g. room temperature, trivacancies may be considered to be essentially immobile.

Clusters larger than three vacancies would be even less mobile than trivacancies. While the configurational energy and mobility of vacancy clusters are important in discussions of excess vacancy decay, we have no method at present to determine experimentally these energies accurately.

7. Production of point defects

We are concerned here with the production of point defects in excess of those present in equilibrium concentrations. The most common ways of generating excess point defects are [93]:

- (1) thermal equilibration and quenching from high temperatures;
- (2) plastic deformation under various conditions;
- (3) damaging the crystal by irradiation with nuclear particles;
- (4) controlled deviations from stoichiometric composition;
- (5) depositing thin films on a cold substrate by evaporation.

As mentioned before, the quenching technique is one of the most powerful methods for studying the vacancies in metals. Its main advantage is that, at least in certain conditions, only vacancies are produced in the metal while both vacancies and interstitials are, in general, created after plastic deformation or irradiation. This section will deal mainly with the quenching technique, with the other methods discussed in less detail. A review about the irradiation technique is reported recently by W. Schilling *et al.* [94].

7.1. Production of point defects by quenching

As described above, thermal equilibrium concentrations of point defects exist at all temperatures. In f c c, b c c and most likely h c p metals, vacancies are the predominant defects existing in thermal equilibrium. The concentration near the melting point T_M is about 10^{-4} , and about 10^{-8} at temperatures near $T_M/2$. Therefore, if a specimen is cooled very rapidly from high temperatures, an excess concentration of vacancies may be retained at low temperatures. The aim of a quenching experiment is, therefore, to quench the specimen from an elevated temperature, T_Q , to a relatively low temperature, rapidly enough to freeze-in the defects present at T_Q . Ideally, it is desirable to freeze-in the entire equilibrium vacancy defect population in an unperturbed state and, after quenching from T_Q , to measure the C_{nV} individually allowing the absolute determination of the various $S_{nV}^F(T)$ and $E_{nV}^F(T)$.

Unfortunately, this aim cannot completely be realized in practice. We shall try to examine in some detail the various problems which arise when one attempts to extract quantitative information on vacancy defects from quenching experiments.

7.1.1. Perturbing effects present in quenching experiments

The following effects can take place during quenching:

- (1) clustering of vacancies during quenching;
- (2) loss of vacancies to sinks such as dislocations during the quench;
- (3) Generation of additional defects by plastic deformation occurring during the quench.

Let us consider these effects in some detail.

7.1.1.1. Clustering of vacancies during quenching.

As the crystal is rapidly cooled, it becomes supersaturated in vacancies which tend to cluster to at least some degree in cases where negative binding energies exist. This effect is impossible to avoid, since the number of jumps required for a given defect to meet another during the quench is generally much smaller than the total number of jumps which the defect could make before being frozen-in during even fast quenches. The number of jumps, m , made by a vacancy in time, t , as given by Cottrell is [95]:

$$m = Zv_0At \exp \left\{ -\frac{E_V^M}{kT} \right\} \quad (7)$$

where Z is the co-ordination number, ν_0 the atomic vibration frequency, and A is an entropy factor.

Lomer [96] studied this problem and estimated a critical temperature. If a specimen is quenched from below this critical temperature, T_c , at a cooling rate dT/dt , vacancies are frozen-in effectively.

Recently, Balluffi *et al.* [97] examined the formation of divacancies from monovacancies during the quenching of an fcc metal. They ignored any defect losses and considered only the redistribution of monovacancies and divacancies. On the basis of the approximate equations:

$$\begin{aligned} \frac{dC_{1V}}{dt} &= -168 \nu C_{1V}^2 \exp\left\{-\frac{E_{1V}^M}{kT}\right\} \\ &+ 28 \nu C_{2V} \exp\left\{-\frac{E_{1V}^M + E_{2V}^B}{kT}\right\}, \\ C_{1V} + C_{2V} &= C = \text{constant}, \\ T &= T(t), \end{aligned}$$

and using the work of Koehler *et al.* [98] concerning an estimate of T_c , and taking into account the calculations carried out by Cotterill [99] for more complicated defect clusters, they concluded:

(1) At least some degree of clustering in the form of small mobile clusters occurs during usual quenching in systems where the clusters possess significant binding energies. The results are relatively insensitive to the quenching rate. The extent of such clustering naturally depends directly upon the properties of the small clusters.

(2) Clusters concentrations become frozen-in rather abruptly at some critical temperature T_c during quenching. An expression for T_c is given by:

$$T_c = \frac{E_{2V}^B \cdot \exp\{(E_{2V}^B + E_{1V}^M)/kT_c\}}{14\nu k T_c \sqrt{(1 + 48 C_{1V} \exp E_{2V}^B/kT_c)}} \left(-\frac{dT}{dt}\right)_{T=T_c}$$

(3) The formation of relatively large immobile clusters may be generally avoided during quenching.

(4) Even if the concentrations of the individual clusters could be measured individually after quenching as a function of quenching rate, attempts to extrapolate the results to an infinite quenching rate in order to obtain the individual cluster concentrations originally present in thermal equilibrium at T_Q would most likely fail.

7.1.1.2. Vacancy losses during quenching. In specimens quenched at finite rates a certain fraction of the supersaturated vacancies is lost at sinks which are present in the specimen during the quench. Possible sinks include the free surface, grain boundaries, subgrain boundaries (dense planar arrays of dislocations), the random three-dimensional dislocation network and the dislocations which may be generated by plastic deformation during the quench. The relative importance of the sinks mentioned above depends, of course, upon their relative densities and the efficiency with which they absorb vacancy defects.

Flynn *et al.* [100], in one of the most complete studies, found that for gold there is a total defect resistivity (concentration) loss which increases as the quenching rate is decreased or the quenching temperature is increased. At sufficiently low quenching temperatures, essentially all losses were avoided by quenching at moderately fast rates. Loss data showing the same general features have been obtained in other investigations with gold [40, 101, 102], platinum [103] and aluminium [50].

Flynn *et al.* [100] showed that a reasonably accurate approximate solution to this problem could be obtained in the form of an eigenfunction expansion, and furthermore, showed that for linear cooling rates the fractional loss of the total vacancy concentration to fixed sinks is a function which depends only on the combined parameter $D_Q T_Q \tau_Q$ where D_Q is the defect diffusivity at T_Q and τ_Q is the time required for the quench. However, in order to calculate actual losses for given types of sinks it is necessary to carry out detailed calculations utilizing the appropriate eigenfunctions. Balluffi *et al.* [97] avoided these complications and calculated defect losses in a typical quenched system by direct numerical integration of the defect diffusion equation in the presence of an appropriate temperature and time dependent boundary condition at the sinks. They concluded the following:

(1) Appreciable vacancy defect losses, primarily to dislocations and to a less extent to subgrain boundaries, generally occur in specimens quenched from elevated temperatures.

(2) A relatively simple model based upon defect diffusion-limited losses to existing dislocations (and subgrain boundaries) is capable of explaining the main features of existing loss data.

(3) Exact calculations of losses are complicated

by: (a) a lack of precise knowledge regarding the sink efficiency of dislocations; (b) possible increases in the dislocation sink density during the quench; and (c) a lack of knowledge of the degree of defect clustering during the quench and the effect of such clustering on the losses.

(4) The method of correcting for defect losses during quenching by different rates and extrapolating the quenched-in increment to infinite rate in order to obtain equilibrium concentrations is a legitimate technique.

7.1.1.3. Effect of quenching strains. A quenched specimen is strained during rapid quenching. There are two causes for this strain. The first is the internal stress, due to differential thermal contraction which is present when the outside of the specimen is cooled relative to the interior; the second is the applied stress due to the hydrodynamic drag which is exerted on the specimen if it is plunged into a liquid-quenching medium. Plastic straining by these means may affect quenching results in two ways: (a) the straining produces unwanted extra point defects and dislocations; and (b) the extra dislocations act as sinks for both the original equilibrium vacancy population and any point defects generated during the quench. The effect of plastic straining may, therefore, be to either increase or decrease the defect concentration obtained after quenching relative to the equilibrium concentration depending upon the relative magnitudes of the two effects described above.

The various possibilities have been investigated extensively by Jackson [104] both theoretically and experimentally. Jackson's results show that the thermally generated strains increase with increased wire diameter, whereas the hydrodynamically induced strains behave in the opposite manner. Furthermore, the thermally generated strains are very small (of the order of 10^{-5}) for specimens with diameters similar to those usually employed in quenching experiments (i.e. 0.04 cm). On the other hand, the hydrodynamic strains may become as large as 3×10^{-3} for wires of diameter near 0.005 cm.

Takamura [43] observed elongation of a specimen due to repeated quenching. Takamura quenched gold wires of various diameters and found that the concentration of quenched-in vacancies depended on the specimen diameter. He estimated the loss of vacancies during quenching, assuming that this loss is inversely proportional to the

cooling rate. He found that the concentration actually quenched into the specimen is larger than the concentration expected when the loss is considered (the equilibrium concentration minus the loss during quenching). In some cases, the total quenched-in concentration increases with the specimen diameter. We would expect the opposite because the cooling rate would be smaller and hence the loss would be larger in the larger specimen. Takamura attributed this effect to the production of vacancies by quenching strains. The plastic strains due to quenching are of the order of 10^{-3} or less and the concentration of vacancies attributed to these quenching strains is of the order of 10^{-5} . Hence the rate of vacancy production would be 10^{-2} or more per unit strain. The rate of vacancy production due to simple tension at low temperatures is of the order of 10^{-4} . The production rate does not increase with the deformation temperature [105]. Therefore, it seems difficult to attribute the Takamura observation simply to the production of vacancies by quenching strains.

Balluffi *et al.* [97] discussed the problem extensively and arrived at the following conclusions:

(1) Thermally induced quenching strains during the water-quenching of normal specimens (diameter ~ 0.041 cm) are small i.e. $\sim 10^{-5}$.

(2) Hydrodynamic stretching strains during the water-quenching of normal specimens are larger, i.e. $\sim 8 \times 10^{-4}$ for diameters ~ 0.041 cm and $\sim 34 \times 10^{-4}$ for diameters ~ 0.005 cm.

(3) The number of vacancies generated by quenching strains is expected to be small relative to the quenched-in ones except for the case of thin specimens quenched into liquid from very low quenching temperatures.

(4) Quenching strains of the order of 10^{-3} may be expected to generate enough dislocations to absorb a significant fraction of the vacancies initially present at elevated quenching temperatures.

(5) At elevated temperatures quenching strains cause a net loss of vacancies, since the sink effect of the dislocations generated is larger than the effect of the extra point defects produced by the deformation.

Finally, we see that it is impossible at present to calculate accurately the number of divacancies and larger vacancy clusters formed during quenching or to discuss the details of probable vacancy production by quenching strains. It is, however, possible to eliminate experimentally the effects due to the

quenching rate and the quenching strains. The extrapolation of the quenched-in vacancy concentration to that for infinite quenching rate is one example. In the experiment of Mori *et al.* [106], however, the effect of quenching strains was not eliminated. Takamura [43] employed wires of various sizes and the results were extrapolated to zero radius. The quenching rate of a wire with zero radius should correspond to an infinite quenching rate and the quenching strains are thus eliminated. Takamura and his co-workers obtained the formation energy of a vacancy to be 0.96 and 0.76 eV in gold and in aluminium, respectively.

7.2. Production of point defects by plastic deformation

Considerable experimental evidence has been accumulated which indicates that point defects are produced by plastic deformation [85, 107–111]. However, it has not yet been firmly established what proportion of vacancies and interstitials are generated and how they are produced during straining. Many models have been proposed for the formation of point defects by moving dislocations. They are based either on the mutual annihilation of dislocations other than screws or on the non-conservative motion of jogs in dislocations with a strong screw component. These models (up to 1962) have been reviewed by Balluffi *et al.* [111], who conclude that a number of models are available to explain defect production either as isolated defects or in the form of rows or platelets. For complete reviews we refer to the papers by Clarebrough *et al.* [112] and van den Beukel [113]. We shall restrict our discussion to some recent papers on the subject.

A problem often considered is whether the point defects produced are vacancies or interstitials or both. If the moving jogs were formed by the intersection of a moving dislocation with a stationary forest dislocation, vacancies and interstitials will be produced in approximately equal numbers. Cottrell [114] showed that if the predominant intersections are between two moving dislocations, the jogs should be mainly of the interstitial type. This conclusion has not been confirmed by Zsoldos [115], who found that the vacancy production is not negligible in this case. When the dislocations are split into partials, construction of the partials at the jog and their behaviour under an applied stress have to be considered. Hirsch [116] concluded that an applied

stress tends to constrict an interstitial producing jog, making it glissile, whereas the vacancy producing jogs will be extended and remain sessile. For that reason point defects formed by low temperature deformation should be predominantly vacancies. Weertman [117] examined the role of partial dislocations attached to a double stacking fault. He concluded that vacancies and interstitials are formed in approximately equal numbers. Pfeffer *et al.* [118] argue that Hirsch and Weertman consider long jogs only, and that the theory cannot be applied to jogs of atomic dimensions (elementary jogs). These authors develop an atomic theory of these elementary jogs, which can dissociate as well as complete dislocations. They show that both vacancies and interstitials can be produced by a non-conservative motion of dissociated elementary jogs. Further, it was found that point defect production will increase with decreasing stacking fault energy.

Friedel [119] doubts whether point defect production by the moving jog mechanism should be important in plastic deformation. He argues that for the rather small dislocation velocities observed during cold work the jogs should move along the dislocation to parts having edge character rather than produce point defects. According to Friedel, in cubic crystals a more important mechanism of point defect production occurs each time a mobile dislocation loop cuts through an attractive tree of the dislocation forest. This model has been worked out in detail by Saada [120]. When a mobile loop meets an attractive tree, the reaction of Hirsch [121] will occur, and the loop will be divided into two parts separated by an immobile junction dislocation. If the Burgers vector of the tree is not parallel to the slip plane of the loop, the two parts of the loop will be in different slip planes. They subsequently bow out until they meet and recombine over a certain length x . It is shown that x is proportional to the size of the dislocation network l :

$$x = Al.$$

It is then easily seen that the concentration of point defects produced is given by

$$C \cong \frac{A}{G} \int_0^{\epsilon} \sigma d\epsilon,$$

where G is the shear modulus and σ and ϵ are the plastic stress and strain respectively. Therefore, the point defect concentration produced by cold-

working would be proportional to the work done.

A different approach was applied by Feltham [122]. His model is that plastic deformation produces a cell structure of dislocations, the cell size decreasing with increasing degree of cold-work. Point defects are produced by non-conservative motion of intersection jogs. The result is that the ratio of point defect concentration, C , and dislocation density Λ is constant during the deformation:

$$\frac{C}{\Lambda} \approx 20 b^2.$$

Feltham compares this result with experimental results of Kovács *et al.* [123] on Ag and Yoshida *et al.* [124] on Al and finds agreement of the observed C/Λ ratio with the calculated $20 b^2$ within a factor of 10. However, Kovács [126] presented a simple model, with experimental proof, which leads to proportionality not only between the plastic work and point defect concentration but also between the plastic work and dislocation density as well.

8. The effect of point defects on the properties of metals

First we shall define two concepts related to the point defects, namely, the "core field" and the "far field" [127]. A localized arrangement of atoms not extending into the lattice in any direction is usually called "point defect". More precisely it can be called the "core field" of the defect comprising typically around 20 atoms. An atomistic treatment is necessary to find the influence of the core field on physical properties of the crystal. A few interatomic distances from the centre of the core field, however, the atomic displacements are usually much smaller than the lattice parameter [91]. This region is called "far field" (Fernfeld) and it extends to the surface of the sample. To describe the far field effects, usually an elastic continuum model of the crystal is used in which the defect is replaced by an arrangement of double forces [128]. For example, the core field governs the scattering of conduction electrons and therefore the electrical resistivity, the far field gives rise to a volume change, and both far field and core field influence the elastic properties.

Many physical properties are sensitive in varying degrees to the presence of point defects, and much of the research in the field stem from a need to know the relation between physical properties and

imperfections in a crystal. Conversely, a structure-sensitive physical property can be used to investigate the nature, concentration, mobility and interaction of defects. For example, point defects, and the distorted regions around them, scatter electrons and neutrons and thus manifest themselves in changes in electrical resistivity and neutron transmission. They also cause change in density, lattice parameter and energy content of the crystal, i.e. stored energy in the solid. Point defects interact with dislocations and thereby cause striking changes in the mechanical properties of a solid.

The physical properties of the crystal can be separated into three groups:

(1) Properties which are approximately proportional to the concentration or number of defects, e.g. the change of the residual electrical resistivity $\Delta\rho$ is equal to the product of the defect concentration, C_D , and the resistivity per unit concentration of defects, ρ_D , which is a specific defect property directly related to the experimental data. It is connected with the more fundamental scattering matrix elements for conduction electrons and thus with the scattering potential, which is based on the particle properties of the core field and the electron wave functions.

Similar physical properties are: internal energy, stored energy, volume, lattice parameter, elastic modulus, internal friction, neutron scattering cross-section, heat conductivity, reciprocal high-field Hall coefficient.

After quenching from high temperatures, single and multiple vacancies are present. The equilibrium concentration of vacancies can be calculated from combined lattice parameters and length measurements, and gives an upper limit of the total quenched-in concentration. The evaluation of specific vacancy properties from high-temperature equilibrium measurements suffers from the uncertainty of the "base line".

(2) Another group of properties is independent of the concentration of the "predominant" defects and provides specific defect properties directly. Mainly transport properties belong to this group: low-field Hall coefficient, relative change of the electrical resistivity in a magnetic field, change of thermopower per resistivity change, relative deviations from Matthiessen's rule.

(3) Finally, physical properties exist which depend in a complicated way on the mean concentration and distribution of the defects in the sample, e.g. partly elastic neutron scattering, magnetic pro-

erties of superconductors, partly internal friction (interaction of defects with dislocations), critical shear stress [129], etc.

To avoid becoming involved in theoretical uncertainties, specific defect properties will be defined which are related as directly as possible to the experimental data (e.g. resistivity per unit concentration). Such defect properties are usually very complex on a theoretical viewpoint. We shall try to mention the relations between some defect properties and their connections with more fundamental solid state parameters where it is possible.

8.1. Transport properties

Transport properties of solids due to the conduction electrons include the electrical resistivity tensor in zero and finite magnetic field, thermal conductivity and thermoelectric power. The transport properties include also phonon thermal conductivity (in connection with the phonon drag part of the thermoelectric power, and in superconductors). We shall discuss some of these properties on the basis of the Boltzmann equation, which is sufficient for the comparatively low defect concentration in quenched metals and which can be solved numerically.

8.1.1. Electrical resistivity in zero magnetic fields

8.1.1.1. Specific electrical resistivity of defects. For non-ferromagnetic cubic crystals with a random distribution of defects, which may have a non-cubic symmetry, the electrical resistivity is a scalar quantity. The contribution of point defects to residual resistivity depends upon the type of defect and on the kind of metal. The extra residual resistivity due to point defects, following Mott and Jones [130], is given by

$$\Delta\rho = \frac{2\pi m v}{n_e e^2} A n; \quad (8)$$

$$A = \int (1 - \cos \theta) I(\theta) \sin \theta d\theta,$$

where m is the electron mass, v the velocity of the electrons at the top of the Fermi surface, n_e the number of free electrons per atom, e the electron charge, n the atomic fraction of defects. A is the effective scattering area, and $I(\theta)$ the intensity of the scattered wave in direction θ . The theoretical determination of the resistivity involves the calculation of A , which can be determined from

scattering theory [31] with the result that for free electron scattering

$$A = \frac{4\pi}{k^2} \sum_l (l+1) \sin^2(\alpha_l - \alpha_{l+1}),$$

where k is the wave number at the Fermi level and is given by $k = 2mv/\hbar^2$, and α_l is the phase shift of order l evaluated from the asymptotic solution of the wave equation. A variety of scattering potentials may be used for the defects but, as shown by Friedel [9], the phase shifts of the plane waves representing the wave functions of the electrons and the charge, Ze required to screen the potential of the defect are related by the equation

$$Z = \frac{2}{\pi} \sum_l (2l+1)\alpha_l. \quad (9)$$

Phase shifts calculated for any particular spherically symmetric potential must, therefore, obey the Friedel sum rule.

TABLE IV Calculated residual resistivity of vacancies in some metals

Metal	Resistivity ($\mu\Omega$ cm/at. %)	References
Aluminium	3.4	[132]
Copper	1.7	[133]
	1.5	[134]
Gold	1.5	[135, 136]
Silver	1.5	[135, 136]

In Table IV we give some calculated values for the residual resistivity of vacancies in metals. Keller [137] carried out a calculation to estimate the resistivity of the vacancy and impurity in nearest-neighbour positions (ρ_{pair}). His result for silver impurities in gold is:

$$\rho_{\text{pair}} = \rho_{\text{vac}} + \rho_{\text{imp}} - 0.1 (\rho_{\text{vac}} \cdot \rho_{\text{imp}})^{1/2},$$

and for zinc in gold it is

$$\rho_{\text{pair}} = \rho_{\text{vac}} + \rho_{\text{imp}} + 0.1 (\rho_{\text{vac}} \cdot \rho_{\text{imp}})^{1/2}.$$

This calculation involved the Born approximation and took into account lattice relaxation effects on the Friedel sum rule; consequently, the results are only approximate.

8.1.1.2. Deviations from Matthiessen's rule (MR).

In most studies of defects in metals, where the electrical resistivity is used as a measure of the defect concentration, MR is assumed to be valid,

which means:

$$\rho = \rho_0(T) + \rho_V \cdot C_V, \quad (10)$$

where ρ_V is the resistivity per unit concentration of vacant lattice sites. Although some deviation from Matthiessen's rule may, in general, be expected, the deviations should be negligible for vacancy defects at 4.2 K. At 78 K, however, small deviations may occur [138, 139]. Under most conditions, changes in residual resistivity may be related closely to the total quenched-in vacancy concentrations.

8.2. Volume and lattice parameter change

In cubic crystals with a random distribution of defects, the following relations hold [140]:

$$\frac{\Delta V}{V} = \frac{3\Delta l}{l} \equiv L = C_V - C_I + C_V \frac{V_V}{V_0} + C_I \frac{V_I}{V_0}, \quad (11)$$

where $\Delta V/V$ is the relative change of volume of a finite sample, $\Delta l/l$ the relative change of length of the sample due to a concentration C_V and C_I of vacancies and interstitials, V_V , V_I are the volume changes of a finite sample due to the lattice distortion in the far field of a vacancy and an interstitial, respectively [141]. The lattice parameter is defined for a homogeneous distribution of defects only, for which a new reference lattice for the crystal can be defined [142]. The relative lattice parameter change $\Delta a/a$ is related to the lattice distortions by

$$3 \frac{\Delta a}{a} \equiv A = C_V \frac{V_V}{V_0} + C_I \frac{V_I}{V_0}. \quad (12)$$

The difference $A - L \equiv C_I - C_V$ is zero only for defect relations in which the number of lattice positions of the sample does not change. From equilibrium measurements of the lattice parameter and length as a function of temperature, v_V cannot be exactly determined since the defect-free value of the thermal expansion (the "base line") is not known accurately enough. A detailed discussion of the subject is given by Seeger [14].

Further information on lattice distortions can be obtained by elastic scattering of neutrons, which react only on lattice disorder. For a detailed discussion of this point and examples on different metals see [127].

8.3. Stored energy

The change of the internal energy of a metal caused by point defects can be divided into two parts (actually the enthalpy is determined in principle, but the difference is negligible for our case):

$$Q = C(E_D^S + E_D^V) = CE_D, \quad (13)$$

where Q is the heat release per atom due to disappearance of C defects per atom, E_D^S the contribution of the static order and E_D^V that of the vibrations and thermal excitations to the stored energy per defect. Interactions between defects are neglected or, if the interaction energy is not negligible, a new defect type is defined (e.g. divacancies etc.).

The stored energy can be measured by a variety of methods. The measurement must be made by measuring the heat released when a crystal, containing defects in excess of the thermodynamic concentration at a given temperature, is annealed at the same temperature to a state in which it contains only the thermodynamic equilibrium concentration of defects. Since in many experiments, such as radiation damage or cold-work, more than one species of point defects is present, it is often desirable to obtain intermediate annealing stages of stored energy and to attempt to relate them to the disappearance of individual defects. The intermediate stages of energy release obtained in this manner cannot be precisely related to the number of defects multiplied by the formation energy because no experimental reference state exists by which the stored energy can be evaluated. Thus, although characteristic annealing curves of stored energy of several defects are informative, the energies of formation thus obtained are not always reliable.

8.4. Mechanical properties

The mechanical properties of metals are influenced in varying degrees by the presence of point defects. A variety of measurements have been used to study these effects which range from changes in the elastic moduli to changes in brittleness, i.e. from the smallest possible measurable strain to mechanical failure. This wide range of conditions is illustrated in Fig. 4 by a schematic stress-strain curve. At small strains the elastic moduli (and elastic susceptibility) and small amplitude internal friction are the characteristic mechanical properties. As the strain is increased, the specimen often exhibits a

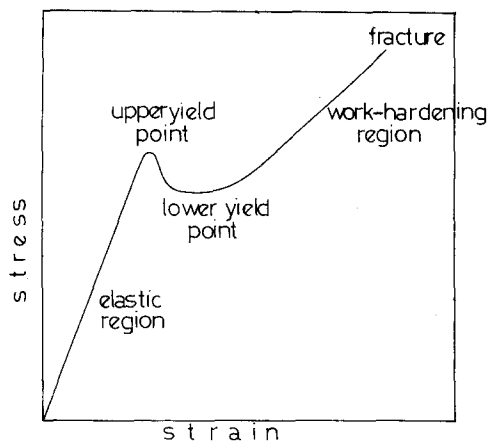


Figure 4 Schematic stress-strain curve for a typical metal, illustrating important mechanical phenomena. (After Damask and Dienes [85]).

yield point followed by a hardening region and eventual fracture. We shall try to discuss the relations between the above mechanical properties and point defects. Many of the ideas involved in these treatments were originally developed for interpreting the influence of impurity atoms, solutes, and precipitation nuclei on the mechanical properties.

8.4.1. Elastic modulus and elastic susceptibility

The reaction of a disordered lattice on applying static or low frequency ($\omega \ll \omega_R$) dynamic stress can be described by the elastic modulus tensor M (ω_R is the resonance frequency due to the defect). The elastic susceptibility χ of the defects is defined as the change of M induced by the presence of the defects and is also a tensor of the same type as M if the defects are distributed at random in the lattice [143]. Three different contributions to χ are distinguished:

(1) Defects can pin dislocations, which causes an increase in M . The best theory of this effect at present is that of Granato and Lücke [144], based on the earlier works of Friedel [145], Koehler [146], and Thompson and Holmes [147]. This theory gives the resulting modulus change by the relation

$$\Delta G/G = K\Lambda \cdot L^2, \quad (14)$$

where Λ is the dislocation density, L is the average dislocation length between pinning points, and K is a constant.

(2) If crystallographically equivalent defect

positions split in energy under the applied strain ϵ , the defects redistribute themselves among the available positions with a certain relaxation time τ . This gives rise to an additional length change and correspondingly to a modulus decrease. The "parelastic" susceptibility χ_p is defined as the difference between the completely "relaxed" and "unrelaxed" modulus.

The relaxation is, in general, correlated with an internal friction which can be used to evaluate the parelastic susceptibility [148].

(3) The elastic susceptibility is analogous to the electric susceptibility. Accordingly, a "dielectric" susceptibility χ_d can be defined, a modulus change which is caused by the change of the density and the atomic interaction potentials of the crystal due to the defects [143].

8.4.2. Internal friction

Excess vacancies affect internal friction in two ways: Zener relaxation and dislocation pinning. Zener relaxation is caused by the atomic rearrangement in an alloy associated with a change in the external stress. The concentration and mobility of vacancies determine the rate of relaxation. Hence, investigations of the Zener relaxation in quenched alloys give information on the properties of vacancies. For the application of the Zener relaxation to the study of vacancies, refer to discussions by Nowick [149], Nowick and Seraphim [150], Cost [151], and Berry and Orehtsky [152].

Excess vacancies interact with dislocations or are annihilated at dislocations to form jogs. Thus, vacancies pin dislocations and thereby reduce their mobility.

Levy and Metzger [153] found that the internal friction due to dislocation motion in aluminium was decreased by quenching. They considered that the quenching effect could not be attributed to quenching strains or to dislocation pinning by impurity atoms. The decrease in internal friction was most satisfactorily explained by quenched-in vacancies which migrated to dislocations and pinned them.

Although internal friction is a useful tool in studying the vacancy-dislocation interaction, there is a disadvantage in that it is so sensitive to the overall condition of the specimen that it may be affected by small amounts of strain introduced by quenching and handling.

8.4.3. Hardening

The development of our understanding of the increase in the yield stress due to rapid quenching (quench hardening) may be divided into two stages. In the first stage, that of the observation of quench-hardening, it was concluded that the aggregation of the quenched-in vacancies in the metal was the main cause of the hardening. This conclusion was confirmed by results from thin foil transmission electron microscopy. In the second stage, the mechanism of hardening was investigated in much greater detail, and the experimental results were compared with observations by transmission electron microscopy of the interaction of dislocations with vacancies and their aggregates.

The experimental results on quench hardening may be summarized as follows:

(1) Pure metals show appreciable hardening when quenched from high temperatures and aged under appropriate conditions. During the ageing, excess vacancies form clusters and/or annihilate at pre-existing dislocations. These effects are responsible for the hardening. In metals in which the vacancy migration energy is low, clustering and condensation may take place to such an extent as to cause hardening during handling after quenching.

(2) No appreciable hardening is observed in polycrystalline specimens tested at room temperature unless aged after quenching. It should be noted here, however, that gold single crystals show appreciable hardening without ageing when tested at liquid helium temperature [154].

(3) Two types of hardening are observed, depending on the quenching temperature. For quenching from high temperatures, age-hardening takes place at a high rate (with a small activation energy), and the amount of hardening increases with the quenching temperature. No over-ageing is observed. For quenching from below a certain temperature (which may depend on the purity of the specimen and the quenching rate), the rate of age-hardening is relatively slow. Over-ageing is observed in copper but not in gold. Mori *et al.* [106] investigated the hardening of gold quenched from 800, 750 and 700° C. In all cases, the yield stress increased in the same manner as observed in specimens quenched from higher temperatures. This appears to be the only difference in the character of quench hardening in copper and in gold.

On the basis of these observations, the mechanism of quench hardening may be considered both in terms of the interaction of dislocations with vacancy clusters and of the jogs formed by condensation of vacancies on dislocations. Interaction of dislocations with dispersed vacancies may be important at low temperatures. A more complete discussion of quench-hardening in metals is given by Kimura and Maddin [45, 155].

8.4.3.1. Mechanism of dislocations-vacancy interactions and quench-hardening. Quenched-in vacancies and vacancy clusters interact with moving dislocations and hinder their motion. In order to calculate the yield stress or critical resolved shear stress of a quench-hardened metal, one must first calculate the yield stress or critical resolved shear obstacle (dispersed vacancies or vacancy clusters of various forms) and the dislocations. If the interaction energy as a function of the distance between the obstacle and the dislocation is known, the interaction force–distance curve can be calculated. Secondly, we must know the distribution of the obstacles, so that the external shear stress necessary to move dislocations through the obstacle may be determined. This stress is then the increase in the critical resolved shear stress by quench-hardening.

Dispersed vacancies, as single vacancies, divacancies and perhaps small voids, interact with dislocations in two ways: the first is where vacancies act as centres of interaction in which the vacancy retains its identity after the dislocation passes by and, the second where vacancies annihilate at dislocations to form jogs on them when the vacancies have been swept up by the dislocations to change their configuration.

Vacancy condensation onto dislocations also occurs during quenching whereby jogs are again formed. The fundamental mechanism of impeding the dislocation motion with jogs should be the same regardless of whether or not the jogs are formed by sweeping vacancies or by condensation of vacancies during quenching (except that the number and size of jogs continuously increases in the former case).

The interaction force between the dislocation and vacancy clusters may be calculated if the stress field around the clusters is known. This calculation is possible in the case of dislocations loops and voids but at present it is possible to calculate only the overall interaction energy for stacking fault tetrahedra.

8.4.3.2. *Solid solution hardening.* We shall deal now with the influence of a second element on the mechanical properties of metals where foreign atoms are assumed to replace some atoms of the matrix. Cottrell [156], Parker and Hazlett [157], Suzuki [158] and Hibbard [159] have described results on polycrystals or on the yield stress of single crystals. Seeger [160, 161] gave a theoretical analysis of the stress-strain curve of pure fcc crystals while Haasen [162] extended this analysis to discuss the effect of alloying. He showed that one reason for alloy-hardening is the change in the mechanism of work-hardening with alloying, i.e. the change in dislocation width, interaction, arrangement, density, etc. No great increase in as-grown dislocation density on addition of solute is observed although it could be expected for very dilute alloys [160, 161]. Most of the change of dislocation arrangement with alloying can be explained in terms of a decrease in stacking fault energy.

In addition to the change of dislocation structure on alloying, there are also direct interactions between solute atoms and dislocations to be considered. These can be subdivided into two groups: (a) dislocation locking: formation of solute atom clouds around dislocations at rest; (b) dislocation friction: effect of solute atoms on moving dislocations. These mechanisms have been described by Haasen [162].

8.4.3.3. *Precipitation-hardening.* The formation of precipitates greatly increases the strength of an alloy. The increase in yield stress depends principally on the strength, structure, spacing, size, shape and distribution of the precipitate particles as well as on the degree of misfit or coherency with the matrix and on their relative orientation. To understand precipitation-hardening one must study in detail the way in which dislocations interact with precipitate particles. Some fundamental investigations of the dislocation precipitate interaction in relatively simple alloys are described in papers by Kelly [163] and Gleiter and Hornbogen [164]. Hardness versus ageing time and X-ray diffraction results on alloys of commercial importance are well documented [165–167].

9. Formation of secondary defects due to quenched-in vacancies

The behaviour of vacancies introduced by quenching has been extensively studied with various

methods such as the measurement of the electrical resistivity change and the direct observation by transmission electron microscopy of secondary defects which are formed by the clustering of vacancies.

Panseri and Federighi [45] and Federighi [168] studied the annealing processes in quenched aluminium by measuring the electrical resistivity. They found two large isolated annealing stages during isochronal annealing. The first stage appeared at about 0° C and the second at about 160° C. The first stage was considered to be a clustering process of vacancies and the second stage a dissociation process of secondary defects. Doyama and Koehler [169] carried out more detailed experiments and discussed this problem further.

Silcox and Whelan [170] and Vandervoort and Washburn [171] studied the substructural change underlying the electrical resistivity change at about 160° C by electron microscopy and concluded this was caused by the disappearance of perfect prismatic loops.

Yoshida *et al.* [172] and Cotterill and Segall [173] reported that a large number of Frank sessile loops were formed together with perfect prismatic loops in quenched super-pure Al, and Kiritani and Yoshida [174] and Kiritani [175] reported that voids were also formed. Yoshida and Shimomura [176] detected a new type of dislocation loops which they inferred were double layer stacking fault loops formed under a certain condition [177, 178].

Doris Kuhlmann-Wilsdorf [179] reported that supersaturated vacancies in crystals may condense into single, double or triple layer disks, parallel to the most closely packed crystal planes. Once such discs exceed a critical diameter, their sides collapse and fuse again. The resultant defects are prismatic dislocations. These are of pure edge character when the collapse takes place without a tangential component. If, on the other hand, the collapse occurs with a tangential offset, which may be required in order to avoid gross faulting, then a partly mixed, partly edge-type dislocation loop results. Shimomura [180] studied further details of the annealing behaviour of secondary defects in quenched pure aluminium by electron microscopy.

In the course of studying small vacancy clusters in quenched face-centered cubic metals, Yoshida and Kiritani [181] defined the so-called “pseudo-

equilibrium" vacancy clusters. They described the change of the state of vacancy clusters during non-equilibrium process of vacancies by introducing the positive (growth) and negative (shrink) reaction ratios. The importance of the detailed analysis which follows the change of the annihilation process of highly supersaturated vacancies is emphasized from the analysis of experiments on the nucleation process of dislocation loops, voids and stacking fault tetrahedra in quenched fcc metals. The analysis indicates that most quenched-in vacancies are retained in small vacancy clusters and are dispersed later and finally absorbed to secondary defects. The latter process is explained on the basis of statistical fluctuations in the cluster size distribution.

9.1. The role of secondary defects in the quench-hardening of Al

9.1.1. Defects responsible for the hardening

The quench-hardening in aluminium is less sensitive to quenching temperatures than that in some other metals including copper and gold. In quenched and aged aluminium, voids [174, 175], dislocation loops, both perfect prismatic loops and Frank sessile loops [173, 178, 182, 183] and heavily jogged dislocations [183] are seen.

The conditions favouring particular defects [175] have to some extent been clarified. The number of loops increases with increasing quenching temperature while the number of voids decreases. Hydrogen atoms in aluminium prevent the voids from collapsing to loops. Frank sessile dislocation loops, rather than perfect loops, are formed if quenching strains are minimized. Hence perfect loops predominate in specimens with rather large diameters while Frank sessile loops predominate in thin wires or foils. Hardening in aluminium can be analysed in terms of both loops and voids.

9.1.2. Resoftening

The recovery of the quench-hardened state has been widely investigated in aluminium. This sort of investigation is useful in identifying the defects responsible for the hardening if a comparison is made by transmission electron microscopy of the defects before and after softening. Rapid disappearance of prismatic loops in quenched aluminium was observed [170, 171] below 200° C and dislocation lines also become straightened at these temperatures.

Kino [184] investigated the resoftening of a

quench-hardened aluminium together with the recovery of the electrical resistivity remaining after low temperature annealing, corresponding to the second stage as defined by Panseri and Federighi [41]. He found that the recovery of the yield stress depended on purity and quenching rate. The recovery of the yield stress in zone-refined high purity aluminium coincided with the recovery of the remaining resistivity and the disappearance of the prismatic loops was related to the hardness in the fully aged specimens. In less pure specimens (99.99%), however, the softening took place in two stages, the first at about 200° C and the second at about 400° C, considered to be due to the stabilization of dislocation loops by impurity atoms. Shin and Meshii [185] investigated the resoftening and elimination of dislocation loops in 99.999 pure aluminium. The loop density decreased rapidly near 100° C, as shown in Fig. 5, while resoftening occurred in two stages, one from 100 to 220° C and the other near 260° C.

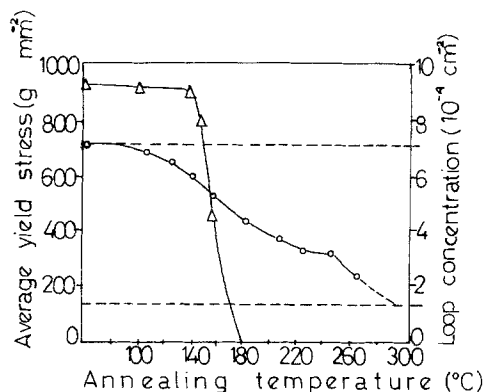


Figure 5 Resoftening of quench hardening in Al and the disappearance of dislocation loops by annealing for 30 min at the temperatures shown. (After Shin and Meshii [185]). \circ , yield stress; Δ , loop concentration; annealing time 30 min.

Instead of loops they found kinked dislocations after annealing above 180° C; which they considered to be formed at the expense of loops. The second stage of resoftening was thought to be due to the straightening of these kinked dislocations which would be stabilized to some extent by impurity segregation.

9.1.3. Main ideas for the loop hardening mechanism

The hardening mechanisms are classified into two groups: temperature-independent and temperature-dependent. Jog formation and intermediate ledge

formation result in temperature-dependent hardening while other mechanisms determine temperature-independent hardening.

For unfaulted loops, the hardening is the sum of the elastic interaction hardening or the junction reaction hardening and the hardening due to jog formation. If dislocations can cross-slip easily, the junction reaction hardening is more important than the elastic interaction hardening.

For faulted loops, the hardening is due to elastic interaction and cutting. The temperature-independent part consists of the elastic interaction and complete ledge formation, and the temperature-dependent part consists of jog formation and the interaction with ledge formation.

At sufficiently low temperatures, the temperature-dependent hardening becomes large and the stress required to cut loops may exceed the stress required to bow and to pass dislocation segments between loops (e.g. the Orowan stress). The yield stress in this case is, of course, determined by the Orowan mechanism and is temperature-independent.

We shall summarize briefly the mechanisms which were reported by Kimura and Maddin [35] on aluminium. The basic experiments were due to Shiotani *et al.* [186] and Westmacott [187].

(1) Temperature-independent hardening due to loops. The observed temperature-independent hardening agrees, within a factor of two or three, with the theory based upon the interaction of loops and dislocations. In aluminium, the junction reaction hardening or the superjog formation seems to be more likely than the simple elastic interaction. There is evidence for the reaction of dislocations with loops.

The observed hardening is usually somewhat larger than that predicted by loop hardening theories. One possible reason for this is that polycrystalline specimens were used in most investigations. The existence of grain boundaries seems to mask a small amount of the hardening. For greater hardening than that due to the presence of grain boundaries, we may neglect grain-boundary effects in the discussion of the yield stress, as in the case of the precipitation hardening phenomena.

(2) Temperature-dependent hardening due to loops. The agreement between theory and experiment is less satisfactory than for temperature-independent hardening. The loop cutting mechanism

predicts too small a value for the yield stress.

It was assumed by Shiotani *et al.* [186] and Westmacott [187] that the temperature-dependence of the yield stress is controlled by a single activation energy. Mori and Meshii [188] emphasized that the deformation in quench-hardened aluminium precedes the formation and growth of slip bands in which dislocation loops are eliminated, and that the contributions of these two processes to the deformation depend on the testing conditions. Certainly, the work-hardening of quench-hardened crystals should be interpreted in the light of both processes.

10. Interactions of point defects

Even during rapid quenches, some of the vacancies reach vacancy sinks and are annihilated there. Matters are further complicated because the meeting of vacancies can lead to divacancies, which in turn may absorb a third and further vacancies to form trivacancies, tetravacancies, and clusters of still higher order. The analysis of this problem is quite complicated. Differential equations to describe the kinetics of vacancies and their aggregates up to and including one type of tetravacancies have been derived [79, 189], but as yet they have only been solved and discussed for a few cases.

10.1. Vacancy condensation on stationary dislocations

For a long time it was believed that a supersaturation of thermal vacancies or interstitials would cause stationary unextended edge or mixed dislocations to climb smoothly, always normal to their slip planes. Lately, however, Kuhlmann-Wilsdorf [190] showed that climb of extended stationary dislocation does not take place in this way. Instead, a preferred nucleation and subsequent growth of prismatic dislocation loops on close-packed planes in contact with pre-existing stationary edge and mixed dislocations seems to be the rule. As a result, jogged dislocations are created instead of smoothly curved ones as originally expected.

A theory which would account for much of the experimental evidence on climbing dislocations was developed from a careful investigation of the binding energy between vacancies and dislocations [191]. It is found that, through the elastic modulus effect, the vacancies are always attracted by the dislocations.

10.2. Vacancy condensation on moving dislocations

Slow moving dislocations, or dislocations which have just stopped moving, appear to be much more efficient sinks for vacancies than stationary ones [183]. Moving dislocations apparently do not climb in the smooth way originally suggested but seem to absorb vacancies mainly through vacancy condensation on the most closely packed places, where the dislocation axis happens to be parallel to those close packed planes [192].

10.3. Interaction between a vacancy and a solute atom

Current theories of solute diffusion in metals require that vacancies have some interaction with solute atoms. Such interaction affects the formation and the migration of vacancies in metals, depending on the valence and the size of the solute atom.

The equilibrium concentration of vacancies in a dilute homogeneous alloy is expressed as [193, 194],

$$C = C_{1V} + C_{VS} \quad (15)$$

where

$$C_{1V} = (1 - ZX) \exp \{S_{1V}^F/k\} \cdot \exp \{-E_{1V}^F/kT\},$$

$$C_{VS} = ZX \exp \{(S_{1V}^F + S_{VS}^B)/k\} \cdot \exp \{-(E_{1V}^F - E_{VS}^B)/kT\}.$$

C_{1V} and C_{VS} are the concentrations of free vacancies and of vacancies bound to solute atoms, respectively, Z is the co-ordination number (12 for fcc and 8 for bcc metals), X is the solute concentration, E_{1V}^F and S_{1V}^F are the formation energy and entropy in the pure metal, and E_{VS}^B and S_{VS}^B are the vacancy-solute binding energy and binding entropy change, respectively. This binding entropy S_{VS}^B is the change in the formation entropy of a vacancy when bound to a solute atom.

For example, when solute atoms having excess ionic charge are introduced into a metal, the neighbouring host atoms are repelled by the Coulomb force in addition to the usual closed-shell repulsion, thereby reducing the binding energy of these atoms. Lazarus [195] has pointed out that such decrease in the energy corresponds to the change in the energy required to form a vacancy at a site adjacent to the solute, which is none other than the binding energy between a vacancy and a solute. Theoretical estimates have also been made of the binding energy by Blatt [196], Alfred and March

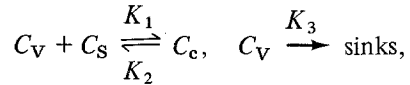
[197], Corless and March [198] and Le Claire [199], but the agreement with experimental diffusion coefficients has been fairly poor.

The theoretical values of E_{VS}^B are very small. Kim *et al.* [200] used a simple Thomas–Fermi screening model to calculate E_{VS}^B in the case of Al–Si alloy. The screened Coulomb field due to the excess charge of the solute $Z_S e$, is given by $V(r) = (Z_S e/r) \exp \{-qr\}$, where q is the Thomas–Fermi screening parameter. Then the vacancy–solute binding energy (the negative of the interaction energy) is

$$E_{VS}^B = -\frac{Z_S \cdot Z_V e^2}{r_0} \exp \{-qr_0\}, \quad (16)$$

where Z_V is the charge of the vacancy and r_0 is the nearest neighbour distance. In this model the vacancy–solute interaction is always attractive ($E_{VS}^B < 0$). For example, in the case of Al–Si alloy $r_0 = 2.86 \text{ \AA}$, $q = 2.12 (\text{ \AA})^{-1}$, $Z_S = 1$ and $Z_V = -3$, we have $E_{VS}^B = 0.35 \text{ eV}$.

Damask and Dienes [85, 201] considered the simple annealing reactions of vacancies to sinks in the presence of solute atoms:



where C_V , C_S , C_c are the concentration of free vacancies, unbound solute atoms and vacancy–solute complexes, respectively, and K 's are the rate constants. From the integration of the corresponding differential equations, they have suggested that the binding energy can be determined from the comparison of the rate constants of annealing of quenched-in vacancies in both pure and impure metals. On these lines, Cattaneo and Germagnoli [202] determined the binding energy between a vacancy and silver atom to be about 0.3 eV for dilute gold–silver alloys.

If the rate of ageing is proportional to the concentration of excess vacancies, the “effective” formation energy of vacancies in an alloy can be determined from the rate of ageing after quenching from high temperatures. Silcox [203] has suggested that the rate of re-ageing after quenching from the reversion temperature can also be used for the same purpose. Thus measurements of the rate of ageing and re-ageing for a wide range of temperatures lead to the evaluation of the apparent formation energy and hence the binding energy. This

principle has been used to determine the binding energies in binary aluminium alloys with or without addition of a small amount of third elements by Panseri and Federighi [204], Turnbull and Cormia [205], Kimura *et al.* [206, 207], Hashimoto and Ohta [208] and other investigators (see, for example, the data collected by Takamura [209]).

Electron microscope observations may also give knowledge on the binding energy. The vacancy–solute binding affects the diffusion rate of vacancies, thereby varying the climb rate of dislocations. Eikum and Thomas [210], and Embury and Nicholson [211] thus estimated the vacancy–magnesium binding energy to be ~ 0.1 to 0.4 and ~ 0.3 to 0.4 eV, respectively. Thomas [212], measuring the vacancy concentration from the density and size of dislocation loops in quenched aluminium alloys, suggested that the binding energies were expected to increase in the order Zn, Mg, Ag, Cu. Alternatively, according to Westmacott *et al.* [213] the order is Zn, Cu, Ag, Mg, Si.

The above results indicate the presence of appreciable binding energies between vacancies and solute atoms. However, they do not necessarily show the true binding energy, since the vacancy–solute binding entropy has been completely ignored and also the assumptions made concerning physical properties (e.g., the electrical resistivity contribution) of the defects involved are not unambiguous. There is, however, a quenching experiment which can give the binding energy as well as the binding entropy change, based on a fairly firm ground [214]. The method consists of achieving an alloy condition in which all vacancies are bound to impurity atoms.

Another type of experiment from which both E_{VS}^{B} and S_{VS}^{B} can be determined correctly, at least in principle, is the measurement of the equilibrium concentration of vacancies in dilute alloys. Precise measurements were made by Beaman *et al.* [215], on the differential length expansions $[(\Delta L'/L') - (\Delta L_0/L_0)]$ and differential X-ray lattice parameter expansions $[(\Delta a'/a') - (\Delta a_0/a_0)]$ between specimens of pure aluminium and the alloys during slow reversible heating and cooling. They used their data to determine absolute differences between the equilibrium vacancy concentrations in the dilute alloys and the pure metal from the relation

$$\begin{aligned} \Delta C_{\text{V}} &= C_{\text{V}}' - C_{\text{V}}^0 = \\ &= 3 \left[\left(\frac{\Delta L'}{L'} - \frac{\Delta L_0}{L_0} \right) - \left(\frac{\Delta a'}{a'} - \frac{\Delta a_0}{a_0} \right) \right], \end{aligned} \quad (17)$$

where the primes and superscript zeros refer to the alloy and the pure metal, respectively. If the vacancy concentration in pure metal, C_{V}^0 is known, the concentration in the alloy, C_{V} , is then determined, from which E_{VS}^{B} and S_{VS}^{B} are obtained.

There are a few attempts to find an empirical relation from the published data for the vacancy–solute binding energy. Hasiguti [216, 217] suggested a relationship consisting of two terms involving the size and the valence of solute atoms in aluminium. However, the position of solute atoms within a group in the periodic table was ignored, and it is difficult to distinguish the difference between solutes as gold and silver which have almost the same size and the same valence. Hasiguti's modified formula is:

$$E_{\text{B}} = E_0 + (Z_{\text{S}} - Z_{\text{Al}})E_{\text{Z}} + \frac{d - d_{\text{Al}}}{d_{\text{Al}}} E_{\text{d}}, \quad (18)$$

where E_{B} is the binding energy, E_0 , E_{Z} and E_{d} are constant with the dimension of energy, Z_{S} and Z_{Al} are the valencies of solute and aluminium atoms respectively, and d and d_{Al} are the atomic diameters of solute and aluminium atoms, respectively.

Doyama [218] considered that the solubility limit of impurities in the matrix might be a good measure of the property of solute atoms, and thus found a relationship for aluminium alloys in a simple form as

$$E_{\text{VS}}^{\text{B}} = -a \log C_{\text{S}} + b \quad (19)$$

where C_{S} is the solute concentration at the solubility limit in the binary alloy system, and a and b are constants. If the solubility at temperature T is expressed in terms of the heat of solution, H , as

$$C_{\text{S}}/(1 - C_{\text{S}}) = A \exp \{-H(1 - 2C_{\text{S}})/kT\},$$

where A is a constant related to the vibrational entropy [219], the following relationship can be obtained by combining with Equation 19:

$$E_{\text{VS}}^{\text{B}} \cong gH,$$

where g is a constant which is $\sim \frac{1}{2}$ [218].

Seeger [220] has suggested that the vacancy–solute binding energy and the binding entropy change can be calculated semi-empirically within the framework of the nearest neighbour interaction in the following way. Consider a vacancy surrounded entirely by solvent (A) atoms in a dilute alloy. If the vacancy is moved to a site at which one of the nearest neighbour atoms is a solute (B) atom, the change in free energy may be given by

the difference in the free energies between A–A and A–B bonds as

$$G = G_{AA} - G_{AB} = -G_B,$$

where G_B is the vacancy–solute binding energy. This simple nearest neighbour interaction model leads to the expressions:

$$E_{VS}^B = (H_A^C - H_B^C - H^S)/Z, \quad (20)$$

$$S_{VS}^B = -\Delta S - (S_A - S_B)/Z,$$

where H^C is the cohesive energy, H^S the heat of solution of solute atoms to the pure metal, ΔS the entropy change due to the solution of a solute atom, S_A and S_B the standard entropies of the pure metals A and B which can be evaluated from thermodynamic data, Z the number of nearest neighbour atoms, respectively. Seeger actually calculated the values of E_{VS}^B and S_{VS}^B for some dilute aluminium alloys, for example, in the case of Al–Zn system, $E_{VS}^B = 0.17$ eV and $S_{VS}^B = 0.35k$.

11. Some general ideas about point defects

To interpret properties of point defects in metals, various theoretical models have been constructed. When looking at a vacancy (Fig. 6) or an interstitial (Fig. 7) in motion through a crystal, one might focus the attention on the nuclei, and try to compute the atomic configurations and the energies involved, assuming simple phenomenological but reasonable interatomic forces and potentials. These forces are related to the electronic structure of the metal, which is locally perturbed, owing to the scattering of electrons by the defects. Thus, as often in solid state physics, simple mechanistic models have been developed in parallel with models which go deeper into the electronic structure of

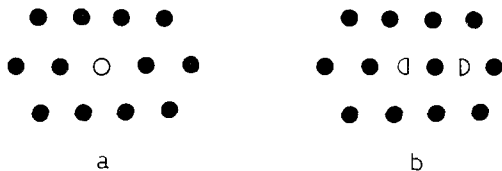


Figure 6 Vacancy: (a) full, (b) split.

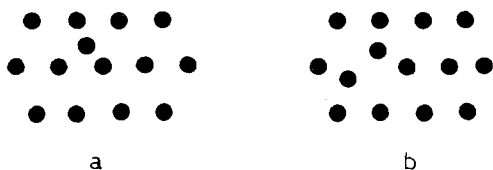


Figure 7 Interstitial: (a) full, (b) split.

the metal.

Friedel analysed both types of model [221]. He concluded that they are often complementary rather than competitive, and also that, at least in some simple cases such as light “normal” metals, there is now some hope of combining the two kinds of approaches into a more self-consistent description. We shall try to give briefly his main ideas.

11.1 Continuum elasticity

The simplest “mechanistic” model treats a defect as a part of an elastic continuous medium but with its own size, form and elastic constants, stuck to the wall of a cavity V , of possibly different size and form. According to this model, the presence of vacancies should not produce any strain. Thus no change in lattice parameter should be observed; the only change in total volume, when a vacancy is created, should come from the atom extracted from the vacant site and added at the surface. Thus the relative decrease in density should be equal to the atomic concentration of vacancies. If anharmonic terms are neglected, the activation volume for vacancy creation should just equal the atomic volume; the activation volume for vacancy motion should be zero.

According to this model the stored elastic energy for a vacancy is zero while for interstitials it is of the order of

$$U \cong \frac{1}{2}E\epsilon^2V, \quad (21)$$

where ϵ is the shear strain necessary to adapt the defect to its cavity and E the corresponding elastic constant. With respect to the coupling between point defects, vacancies and full interstitials have no elastic interactions. They attract each other with a force varying as r^{-7} .

More realistic model is obtained for a vacancy if it is treated as an elastic inhomogeneity [191].

11.2. Model interatomic potentials

To construct a model suitable for defect calculation a lattice energy function must be defined. This function depends on the position of all the atoms in the lattice.

These models usually assume that the lattice energy can be split into a sum of pair potentials, the atoms interacting with each other by two body forces which depend only on the interatomic distance with a long-range exponential decrease which affects only very few neighbours (Fig. 8a and b, [222]).

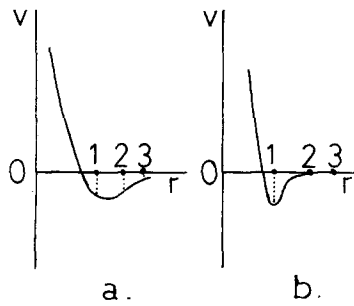


Figure 8 Schematic illustration of pair interaction potentials $V(r)$. (a) Form in common use; (b) very short-range form.

The main two body forces are generally applied only within a small part of the crystal, and the effect of the remaining part can be taken into account by suitable boundary conditions. A detailed description of the subject is recently given by Johnson [223].

This leads to the problem of the boundary conditions. The main interest of such computations is to give a detailed description of the atomic distribution in the immediate neighbourhood of the defect and for this, a microcrystal of typically 2000 to 3000 atoms is considered. Defects are introduced near its centre and only push the self-consistency of the computed displacements far enough from the defect to be within their limits of accuracy. In most cases, the size of the computed relaxed zone is definitely smaller than the size of the crystal. It is then clear that the exact nature of the boundary conditions is of no importance. The surface atoms can be free to move or be blocked on their lattice positions. But it is also clear that such computations cannot give any results on the long range distortions, or on the activation volumes of the defects. To describe more correctly these long range strains, intermediary models have sometimes been used [224], where a very few atoms at the core of the defect have been treated by pair potentials. This core interacts elastically with the surrounding matrix, which is treated as an elastic continuum.

To construct reasonable pair potentials they are adjusted to match various physical properties of the metal. For example the widely used Morse potential:

$$V(r) = D[\exp\{-2\alpha(r-r_0)\} - 2\exp\{-\alpha(r-r_0)\}] \quad (22)$$

contains three numerical parameters D , α , r_0 , which can be determined as follows. For this potential,

the total lattice energy ϕ is given by

$$\phi = \frac{1}{2}ND \sum_j [\exp\{-2\alpha(r_j-r_0)\} - 2\exp\{-\alpha(r_j-r_0)\}],$$

where r_j is the distance from the origin to the j th atom, and N is the total number of atoms in the lattice.

If this energy is calculated for a crystal with $r_j = M_j a$, where a is the experimental value of the lattice parameter, then it must be equal to the experimental energy of sublimation E_S , extrapolated to zero temperature and pressure, that is

$$\phi(a) = E_S(a).$$

The equilibrium condition requires that

$$\left(\frac{d\phi}{dr}\right)_a = 0.$$

Finally it can be shown that ϕ is related to the compressibility K_B as:

$$\frac{1}{K_B} = \left(V \frac{d^2\phi}{dr^2}\right)_a.$$

With the use of these three equations the numerical values of the constants have been determined for many metals [225].

11.3. Electronic structure

The first treatments of scattering by point defects consider the valence electrons of the metal as free and neglect the details of its atomic structure. As for impurities in general, one can distinguish three factors, valence, period and size, and assume that the first predominates [226].

It is usually sufficient to treat this scattering within first order perturbation. Owing to this "valence" effect, the scattering by a vacancy or an interstitial is roughly equivalent to the valence of the metal.

The lattice distortions around the defects thus alter the scattering in two ways:

(1) the local concentration or dilatation alters the local density of ionic charge, thus the effective valency of defect (so called Harrison-Blatt correction [227]);

(2) the local variations of strain can cause similar effect to phonon scattering.

Both these effects cause only slight corrections; therefore, the residual resistivity of vacancies and interstitials should be comparable, and correspond

to scattering cross-sections of atomic dimensions.

The formation energy for vacancies should be directly related to the Fermi energy, a result which gives reasonable values only for monovalent metals [8].

Finally, as for any local imperfections, the self-consistent perturbing potential $V(r)$ around a point defect should die out at long range with oscillations which are related to the Fermi wavelength (Fig. 9). Within the first order perturbation scheme the

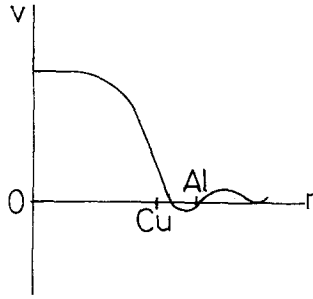


Figure 9 Perturbing potential due to a vacancy in a free electron model. (After Déplanté and Blandin [228]).

following summary [228] can be made:

(1) the value of V at the neighbour distance b gives the electronic part of the energy of interaction with substitutional impurities;

(2) the slope $(dV/dr)_{r=b}$ at that distance gives the force acting on the neighbours due to the presence of the defects; and

(3) the curvature $(d^2V/dr^2)_{r=b}$ gives the change of elastic constants due to the defects.

12. Some annealing equations describing the behaviour of vacancies in quenched metals

At low quenched-in vacancy concentrations, where one would expect simple annihilation of monovacancies at inexhaustible sinks, small amounts of highly mobile defect clusters, e.g. divacancies, can have no marked effect upon the annealing kinetics. At high vacancy concentrations, the clustering of vacancies becomes important and small amounts of impurities have significant effects on annealing behaviour. If we consider a simple system in which monovacancies are the only point defects present, the vacancies anneal out at dislocations, grain-boundaries, etc. This problem may be treated simply by applying the chemical rate equation in the form [229, 230]:

$$dC_{1V}/dt = -\alpha D_{1V} \cdot C_{1V},$$

where C_{1V} and D_{1V} are the concentration and the diffusion coefficient of monovacancies, and α is a geometrical factor. The solution of this equation gives a simple exponential vacancy decay, namely,

$$C_{1V}(t) = C_{1V}(0) \cdot \exp \{-\alpha D_{1V} t\}.$$

Another way of approaching the above problem is to make use of diffusion theory, treating the whole crystal as a continuum but taking into account a concentration gradient near the sinks. We have then

$$\frac{\partial C_{1V}(x, t)}{\partial t} = D_{1V} \cdot \nabla^2 C_{1V}(x, t).$$

In general, the solutions can be represented as a sum of exponentials with different time constants τ_m .

If we consider divacancies also, we may set up the differential equations

$$dC_{1V}/dt = 2K_2 C_{2V} - 2K_1 C_{1V}^2 - K_3 C_{1V},$$

$$dC_{2V}/dt = K_1 C_{1V}^2 - K_2 C_{2V} - K_4 C_{2V},$$

where K_n are reaction constants. If only interactions between nearest neighbours are considered, the K 's are written as

$$K_1 = 84\nu_{1V}^M \cdot \exp \{-E_{1V}^M/kT\},$$

$$K_2 = 14\nu_{2V} \cdot \exp \{-(E_{2V}^M + E_{2V}^B)/kT\},$$

$$K_3 = \alpha_1 D_1 \quad \text{and} \quad K_4 = \alpha_2 D_{2V}.$$

K_1 determines the formation rate of V_2 and K_2 , the dissociation rate of V_2 , α_n is a function of the sink density, and the ν is a frequency factor.

Generally, the equations which describe the microscopic behaviour of the sample are complicated. In the resistivity measurements on fcc metals Koehler [231] wrote these equations as:

$$\Delta\rho = a_1 c_1 + a_2 c_2 + a_3 c_3 + \dots + a_n c_n + \dots,$$

where the $c_i(r, t)$ represent the fractional concentrations of the various defects present. The a_i is a measure of the contributions of the various defects to the resistivity. Changes of defect concentrations with space and time are described by a series of coupled differential equations, usually non-linear, which were given by Doyama [76].

13. Conclusions

In this review an attempt has been made to discuss briefly some of the more important aspects of the

characteristics and behaviour of point defects in metals. Some large areas, including the role of point defects in high temperature deformation and in irradiation damage, have been deliberately omitted. The review has mainly been concentrated on vacancies since these defects play a major role in many physical processes of technological importance. Although very significant progress has been made over the past 25 years, it is clear that many questions remain unanswered both from theoretical and experimental points of view.

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