

## VACANCY–SOLUTE INTERACTIONS IN METALS

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This review includes the experimental techniques for the determination and theoretical calculations of vacancy–solute interactions. As an introduction, phenomenological treatments are presented. Thermal equilibrium concentrations of vacancy–solute pairs, apparent formation energies of a vacancy and formation of vacancy–solute atom pairs during quenching and aging are discussed. The experimental techniques included are thermal equilibrium techniques by the simultaneous measurement of length and lattice parameter changes and by positron annihilation, impurity diffusion at high temperatures, quenching experiments and aging processes. The theoretical calculations of the binding energies between a vacancy and a solute atom are critically reviewed. Elastic method, the pseudopotential method, and the screening potential method are included. Proposed semi-empirical rules are also reviewed.

Cette revue critique comprend les techniques expérimentales permettant de déterminer les interactions lacune-soluté et les calculs théoriques correspondants. En introduction, les traitements phénoménologiques sont présentés. Les concentrations de paires lacune-soluté à l'équilibre thermique, les énergies de formation apparentes d'une lacune et de formation de paires lacune-atome de soluté durant la trempe et le vieillissement sont discutées.

Les techniques expérimentales présentées sont les techniques d'équilibre thermique par mesure simultanée des variations de longueur et de paramètre cristallin et par annihilation de positrons, la diffusion des impuretés à haute température, les expériences de trempe et les processus de vieillissement.

Les calculs théoriques des énergies de liaison entre une lacune et un atome de soluté sont passées en revue de façon critique. La méthode élastique, la méthode du pseudopotentiel et la méthode du potentiel d'écran sont également incluses. Enfin les règles semi-empiriques proposées sont également passées en revue.

Dieser Überblick beinhaltet die experimentellen Bestimmungsmethoden und die theoretischen Rechnungen für die Leerstelle-Fremdatom-Wechselwirkung. Als Einleitung wird eine phänomenologische Behandlung mitgeteilt. Die Konzentration von Leerstelle-Fremdatom-Paaren im thermischen Gleichgewicht, die scheinbare Bildungsenergie einer Leerstelle und die Bildung von Leerstelle-Fremdatom-Paaren während der Abschreckung und Auslagerung werden diskutiert. Die experimentellen Methoden sind thermische Gleichgewichtsmethoden durch gleichzeitige Messung der Längen- und Gitterkonstantenänderung und durch Positronenvernichtung, ferner Fremddiffusion bei hohen Temperaturen und Abschreck- und Auslagerungsexperimente. Die theoretischen Rechnungen für die Bindungsenergie zwischen einer Leerstelle und einem Fremdatom werden kritisch überprüft. Sie umfassen die elastische Methode sowie die Pseudopotential- und die Abschirmpotentialmethode. Vorgeschlagene halbempirische Beziehungen werden ebenfalls überprüft.

### 1. Introduction

Vacancies play an important role for the diffusion of atoms in crystalline solids. Substitutional impurity atoms and alloying element atoms also diffuse with the aid of vacancies. When a vacancy comes to one of the neighboring lattice sites of a substitutional impurity atom, the impurity atom can migrate. The impurity atom often moves easier when the binding energy between the impurity atom and a vacancy is large. Therefore the interaction between a substitutional impurity atom and a vacancy is quite important not only in the

studies of basic properties of lattice defects but also in the study of practical applications such as G.P. zone formation, precipitation, and heat treatment of alloys. A few review papers have been published [1–4].

### 2. Concentration of vacancies in dilute alloys

The thermal equilibrium fractional concentration  $c_v$  of vacancies in a pure metal can be written as

$$c_v = \exp(S_v^F/k) \exp(-E_v^F/kT) = A_v \exp(-E_v^F/kT), \quad (1)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature,  $E_V^F$  the formation energy of a vacancy and  $S_V^F$  the formation entropy of a vacancy which is associated with the vibrational frequency change due to the formation of a vacancy.  $A_V$  is called the pre-exponential factor.  $S_V^F$  is about  $1.5 k$  for close packed metals [5,6] and is a function of the  $c/a$  ratio for the hexagonal structure [6].

In a dilute alloy the thermal equilibrium fractional concentration of vacancy-substitutional impurity pairs  $c_{vi}$  is given by

$$c_{vi} = A_{vi} Z c_i \exp \left( -\frac{E_V^F - B_{vi}}{kT} \right), \quad (2)$$

where  $Z$  is the coordination number,  $c_i$  is the fractional concentration of substitutional impurity atoms,  $B_{vi}$  is the binding energy between a vacancy and a substitutional impurity atom, and  $A_{vi}$  is the entropy factor. The thermal equilibrium fractional concentration of free vacancies which are not at the nearest neighbor sites of impurity atoms is

$$c_v = A_v \{1 - (Z + 1) c_i\} \exp(-E_V^F/kT). \quad (3)$$

The total fractional concentration of vacancies in thermal equilibrium is then [7]

$$c_t = c_v + c_{vi} = \left[ A_v \{1 - (Z + 1) c_i\} + A_{vi} Z c_i \exp \left( \frac{B_{vi}}{kT} \right) \right] \exp \left( -\frac{E_V^F}{kT} \right), \quad (4)$$

This equation can be written as

$$c_t = A_A^F(T) \exp[-E_A^F(T)/kT]. \quad (5)$$

Then,  $A_A^F(T)$  and  $E_A^F(T)$  are functions of the absolute temperature. Hereafter these are called the apparent pre-exponential factor and the apparent formation energy of a vacancy, respectively. It is easily found that

$$E_A^F = E_V^F - f(T), \quad (6)$$

where

$$f(T) = -\frac{B_{vi} Z c_i \beta \exp(B_{vi}/kT)}{1 - (Z + 1) c_i + Z c_i \beta \exp(B_{vi}/kT)} \quad (7)$$

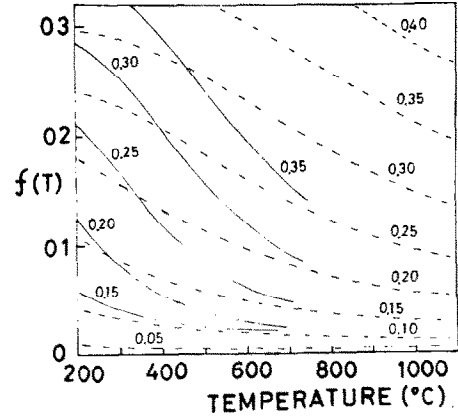


Fig. 1. Difference between the formation energy of a vacancy in pure metals and dilute alloys. Solid lines are for  $c_i = 1 \times 10^{-3}$  and broken lines are for  $c_i = 5 \times 10^{-3}$ . Numbers are  $B_{vi}$  in eV.

and

$$\ln A(T) = \frac{S_V^F}{k} + \ln \left[ 1 - (Z + 1) c_i + Z c_i \beta \exp \left( \frac{B_{vi}}{kT} \right) \right] - \frac{f(T)}{kT}, \quad (8)$$

in which

$$\beta = \exp \left( \frac{S_{vi}^F - S_v^F}{k} \right), \quad (9)$$

The function  $f(T)$  is plotted in fig. 1 for the cases of  $c_i = 10^{-3}$  and  $5 \times 10^{-3}$  assuming  $\beta = 1$ . It is important to note that  $f(T)$  is not a function of  $E_V^F$ , therefore this figure can be used for any metal.

### 3. Kinetic equations

The kinetic equations governing the rate of change of the fractional concentrations of vacancies,  $c_v$ , vacancy-impurity pairs,  $c_{vi}$ , and free impurity atoms,  $c_i$  are

$$dc_v/dt = -\beta_1 c_v c_i + \beta_2 c_{vi} - D_v \nabla^2 c_v, \quad (10a)$$

$$dc_{vi}/dt = \beta_1 c_v c_i - \beta_2 c_{vi} - D_{vi} \nabla^2 c_{vi}, \quad (10b)$$

$$dc_i/dt = -\beta_1 c_v c_i + \beta_2 c_{vi}, \quad (10c)$$

where

$$\beta_1 = \eta_1 \nu_1 \exp(-E_V^M/kT)$$

and

$$\beta_2 = \eta_2 \nu_2 \exp[(-E_V^M + B_{vi})/kT] . \quad (11)$$

$\eta_1$  is 84 for fcc metals and 56 for bcc metals.  $\eta_2$  is 7 for fcc and bcc metals.  $\nu_1$  is the vibrational frequency of an atom next to a vacancy and  $\nu_2$  is the vibrational frequency of a solute atom next to a vacancy associated with a substitutional impurity atom. At thermal equilibrium the last terms of eqs. (10a) and (10b) and also  $dc_v/dt$  and  $dc_{vi}/dt$  vanish. Then

$$c_{vi} = \frac{\beta_1}{\beta_2} c_v c_i = \frac{\eta_1 \nu_1}{\eta_2 \nu_2} c_v c_i \exp\left(\frac{B_{vi}}{kT}\right) = \eta_3 c_v c_i \exp\left(\frac{B_{vi}}{kT}\right) \quad (12)$$

is obtained. Here  $\eta_3 = 12\nu_1/\nu_2$  for a fcc structure. Eq. (12) should be compared with eq. (2). This relation can also be obtained from statistical thermodynamics. The kinetic equations (10) have been criticized by Koiwa. He treated this problem more rigorously [8].

#### 4. Formation of vacancy-impurity atom pairs during quenching

Quenching is a quite important heat treatment of commercial alloys. Metallurgists often ignore the change of the states of lattice defects during quenching, particularly vacancies, and misunderstand the quenched

state, particularly from the point of view of vacancies.

When a specimen containing impurity atoms is quenched from a high temperature, vacancies migrate forming vacancy-impurity pairs during quenching even though the quench rate is fast. Numerical analyses can be made by integrating the kinetic equations (10a, b, and c) [9]. The results are shown in fig. 2. At higher temperatures vacancies can migrate quite fast and the break-up of vacancy-impurity pairs also frequently occurs, so that the thermal equilibrium between vacancies and vacancy-impurity pairs is maintained above a temperature  $T_{vi}^*$ .  $T_{vi}^*$  is called the critical temperature. Below  $T_{vi}^*$  the migration of vacancies is so slow that the formation of vacancy-impurity pairs is almost stopped. At the critical temperature  $T_{vi}^*$

$$\begin{aligned} \left(\frac{dT}{dt}\right)_{T=T_{vi}^*} &= -\frac{\beta_1 k T_{vi}^{*2}}{\eta_3 B_{vi}} \left[ \eta_3 (c_i + c_v) + \exp\left(-\frac{B_{vi}}{k T_{vi}^*}\right) \right] \\ &= -\frac{\eta_2 \nu_2 k T_{vi}^{*2}}{B_{vi}} \exp\left(\frac{E_V^M}{k T_{vi}^*}\right) \left[ \eta_3 (c_i + c_v) \right. \\ &\quad \left. + \exp\left(-\frac{B_{vi}}{k T_{vi}^*}\right) \right] . \end{aligned} \quad (13)$$

The numerical values of  $T_{vi}^*$  can be much more easily found from eq. (13) compared with integrating eq. (10). The critical temperature  $T_{vi}^*$  is a function of the fractional concentrations of vacancies and impurity atoms, the binding energy between a vacancy and an impurity atom, the activation energy of migration of a vacancy, and the cooling rate. Using  $T_{vi}^*$  the fractional concentration of vacancy-impurity atom pairs just after quenching,  $(c_{vi})_0$ , can easily be calculated [9]. The annihilation of vacancies to sinks during quenching

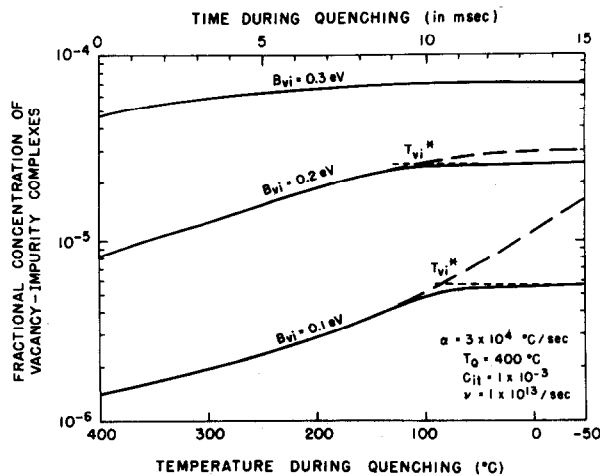


Fig. 2. The change of vacancy-impurity pairs during quenching in dilute aluminum alloys,  $c_{it} = 10^{-3}$ .

Table 1

Values of the critical temperature  $T_{vi}^*$  in aluminum (in °C) [9]

Binding energy (eV)	Quenching rate $10^4$	°C/s ( $c_i=10^{-3}$ , $c_t=10^{-5}$ )	
		$2 \times 10^4$	$5 \times 10^4$
0.01	2	8	17
0.02	12	18	27
0.03	19	26	35
0.05	32	40	49
0.07	42	50	60
0.10	56	64	76

is not very important in the calculations of  $T_{vi}^*$ . Only the total concentration of vacancies present at  $T_{vi}^*$  is important (see table 1).

### 5. Experimental determination of the binding energy between a vacancy and a substitutional impurity atom, $B_{vi}$

Many methods to determine the binding energy between a vacancy and a substitutional impurity atom are based upon measurements of a property connected to the total concentration of vacancies and obtain the apparent formation energy of a vacancy either by thermodynamic equilibrium experiments or by quenching experiments.

#### 5.1. $\Delta l/\Delta a$ measurement

The absolute fractional concentration of vacancies in a specimen can be determined by measuring the macroscopic length change ( $\Delta l$ ) and lattice parameter change ( $\Delta a$ ) simultaneously in the same specimen with and without vacancies. Let the formation volumes of a single vacancy and a vacancy–impurity pair by  $V_V^F$  and  $V_{vi}^F$ , respectively, and the atomic volume  $\Omega$ , then

$$\frac{\Delta a}{a} = \frac{c_v}{3} \left( \frac{V_V^F}{\Omega} - 1 \right) + \frac{c_{vi}}{3} \left( \frac{V_{vi}^F}{\Omega} - 1 \right),$$

$$\frac{\Delta l}{l} = \frac{c_v V_V^F}{3\Omega} + \frac{c_{vi} V_{vi}^F}{3\Omega}.$$

From these, the relation

$$c_v + c_{vi} = 3 \left( \frac{\Delta l}{l} - \frac{\Delta a}{a} \right) \quad (14)$$

can be obtained. This method has been suggested by Eshelby [11] and successfully applied to pure metals by Simmons and Balluffi [11–14] and others [15,16]. The method was applied to dilute aluminum alloys [17–20] and lead alloys. [21]. The binding energies between a silver atom and a vacancy and a magnesium atom and a vacancy in aluminum determined by Beaman, Balluffi and Simmons are 0.08 eV and  $\leq 0.01$  eV, respectively. Feder and Nowick [21] reported no appreciable change in vacancy concentrations in Pb–1% In, and Pb–5% Tl compared with pure lead. Burke and King obtained the values of  $B_{vSi}$  (in Al) and  $B_{vCu}$  (in Al)

to be 0.03 eV [19,4] and 0.00 eV [20,4].

The resolution in measuring the change of lattice parameter and macroscopic length is almost of the order of  $10^{-5}$ . Therefore a fairly high concentration of impurity has to be added to the specimens. The criticism of this method is concerned with the difference between the clustering and dispersion of impurity atoms at low and high temperatures. Recently neutron diffraction and lasers are being used to obtain higher accuracy.

#### 5.2. Positron annihilation

The kinetic energy of a positron emitted from nuclear decay is of the order of 1 MeV but reduced to the order of  $kT$  (where  $k$  is the Boltzmann constant and  $T$  is the specimen temperature in the absolute scale) within a very short time (order of  $10^{-12}$  s) after making inelastic collisions. The “thermalized” positron travels in the metal with a kinetic energy of the order of  $kT$  and finally annihilates with an electron emitting in most cases two gamma rays nearly in opposite directions. In the annihilation process the energy and momentum of the total system are conserved. The total momentum of the two gamma rays is the sum of the momenta of the electron and positron annihilated. The momentum of the annihilated positron can be ignored because the positron is normally much slower than electrons.

A vacancy in a metal is formed by extracting a positive ion and putting it on a surface, therefore a vacancy is electronically negatively charged compared with the perfect region. A positron is positively charged and a vacancy is negatively charged, therefore a positron is attracted and trapped by a vacancy due to the Coulomb interaction. A vacancy is negatively charged compared with the perfect region, therefore some conduction electrons are pushed away. In other words the conduction electron density is less at a vacancy site compared with other lattice sites. Since a positron annihilates an electron, the lifetime of a positron is roughly proportional to the electron density; therefore the positron trapped by a vacancy lives longer than a free positron. The angular correlation curve using a long slit geometry consists of, roughly speaking, two parts, the parabolic part due to the annihilation with conduction electrons and the gaussian part due to the annihilation of core electrons. In a vacancy there is

of course no ion, that is low core electron density; therefore the positron trapped by a vacancy has more chance to annihilate conduction electrons. Therefore the  $\gamma$ - $\gamma$  angular correlation of annihilation radiation emitted by positrons trapped by a vacancy is apparently narrower and the peak counting rate is higher.

The kinetic equations are very similar to those of vacancy trapping by impurity atoms:

$$dn_f/dt = -\lambda_f n_f - \eta_v c_v n_f - \eta_{vi} c_{vi} n_f, \quad (15a)$$

$$dn_v/dt = -\lambda_v n_v + \eta_v c_v n_f \quad (15b)$$

and

$$dn_{vi}/dt = -\lambda_{vi} n_{vi} + \eta_{vi} c_{vi} n_f, \quad (15c)$$

where  $n_f$ ,  $n_v$  and  $n_{vi}$  are the numbers of free positrons, positrons trapped by a vacancy and trapped by a vacancy-impurity pair, respectively,  $c_v$  and  $c_{vi}$  are the fractional concentrations of free vacancies and vacancy-impurity pairs, and  $\lambda_f$ ,  $\lambda_v$  and  $\lambda_{vi}$  are the annihilation rates of free positrons, positrons trapped by a vacancy and trapped by a vacancy-impurity pair, respectively.  $\mu_v$  and  $\mu_{vi}$  are the trapping rates of positrons by a vacancy and a vacancy-impurity pair. Here the detrapping of positrons from the trapped state is ignored. The solutions of eqs. (15) are

$$n_f = n_f(0) \exp(-\Gamma t), \quad (16a)$$

$$n_v = \left( n_v(0) + \frac{\mu_v c_v n_f(0)}{\Gamma - \lambda_v} \right) \times \exp(-\lambda_v t) - \frac{\mu_v c_v n_f(0)}{\Gamma - \lambda_v} \exp(-\Gamma t) \quad (16b)$$

and

$$n_{vi} = \left( n_{vi}(0) + \frac{\mu_{vi} c_{vi} n_f(0)}{\Gamma - \lambda_{vi}} \right) \times \exp(-\lambda_{vi} t) - \frac{\mu_{vi} c_{vi} n_f(0)}{\Gamma - \lambda_{vi}} \exp(-\Gamma t), \quad (16c)$$

where

$$\Gamma = \lambda_f + \mu_v c_v + \mu_{vi} c_{vi}. \quad (16d)$$

When the lifetime spectrum is analyzed assuming that the spectrum is composed of the sum of the three exponential decay terms, the decay rates are  $\Gamma$ ,  $\lambda_v$  and  $\lambda_{vi}$ , where  $\Gamma$  is not a constant but changes with the

fractional concentrations of vacancies and vacancy-impurity atom pairs. The intensities of the components are

$$I_1 = \left( 1 - \frac{\mu_v c_v}{\Gamma - \lambda_v} - \frac{\mu_{vi} c_{vi}}{\Gamma - \lambda_{vi}} \right) n_f(0), \quad (17a)$$

$$I_2 = n_v(0) + \frac{\mu_v c_v n_f(0)}{\Gamma - \lambda_v}, \quad (17b)$$

and

$$I_3 = n_{vi}(0) + \frac{\mu_{vi} c_{vi} n_f(0)}{\Gamma - \lambda_{vi}}. \quad (17c)$$

Analyzing the positron lifetime spectrum and using eqs. (16),  $\lambda_f$ ,  $\lambda_v$ ,  $\lambda_{vi}$ ,  $\mu_v c_v$  and  $\mu_{vi} c_{vi}$  can be determined. Usually  $n_v(0)$  and  $n_{vi}(0)$  can be chosen as zero. If we further assume that  $\mu_v = \mu_{vi}$  and  $\lambda_v = \lambda_{vi}$ , then

$$I_1 = \left( 1 - \frac{\mu_v (c_v + c_{vi})}{\Gamma - \lambda_v} \right) n_f(0) \quad (18a)$$

and

$$I_{2+3} = \frac{\mu_v (c_v + c_{vi})}{\Gamma - \lambda_v} n_f(0), \quad (18b)$$

where

$$\Gamma = \lambda_f + \mu_v (c_v + c_{vi}), \quad (18c)$$

Doyama showed that in normal experimental conditions [22]

$$\lambda_f n_f + \mu_v c_v n_f + \mu_{vi} c_{vi} n_f = N, \quad (19a)$$

$$\mu_v c_v n_f = \lambda_v n_v \quad (19b)$$

and

$$\lambda_{vi} n_{vi} = \mu_{vi} c_{vi} n_f, \quad (19c)$$

where  $N$  is the number of positrons emitting into a specimen per second. Then

$$n_f = \frac{N}{\lambda_f + \mu_v c_v + \mu_{vi} c_{vi}} = \frac{N}{\Gamma}, \quad (20a)$$

$$n_v = \frac{\mu_v c_v n_f}{\lambda_v} = \frac{\mu_v c_v N}{\lambda_v (\lambda_f + \mu_v c_v + \mu_{vi} c_{vi})} = \frac{\mu_v c_v N}{\lambda_v \Gamma}, \quad (20b)$$

and

$$n_{vi} = \frac{\mu_{vi} c_{vi} n_f}{\lambda_{vi}} = \frac{\mu_{vi} c_{vi} N}{\lambda_{vi} (\lambda_f + \mu_v c_v + \mu_{vi} c_{vi})} = \frac{\mu_{vi} c_{vi} N}{\lambda_{vi} \Gamma}. \quad (20c)$$

The fractions of gamma-rays emitted from free positrons, positrons trapped by vacancies, and vacancy-impurity atom pairs are

$$\eta_f = \frac{\lambda_f n_f}{\lambda_f n_f + \lambda_v n_v + \lambda_{vi} n_{vi}} = \frac{\lambda_f}{\lambda_f + \mu_v c_v + \mu_{vi} c_{vi}}, \quad (21a)$$

$$\eta_v = \frac{\lambda_v n_v}{\lambda_f n_f + \lambda_v n_v + \lambda_{vi} n_{vi}} = \frac{\mu_v c_v}{\lambda_f + \mu_v c_v + \mu_{vi} c_{vi}}, \quad (21b)$$

and

$$\eta_{vi} = \frac{\lambda_{vi} n_{vi}}{\lambda_f n_f + \lambda_v n_v + \lambda_{vi} n_{vi}} = \frac{\mu_{vi} c_{vi}}{\lambda_f + \mu_v c_v + \mu_{vi} c_{vi}}. \quad (21c)$$

The height of the peak counting rate of angular correlation  $N(0)$  is written as

$$N(0) = N(0)_f \eta_f + N(0)_v \eta_v + N(0)_{vi} \eta_{vi}, \quad (22)$$

where  $N(0)_f$ ,  $N(0)_v$  and  $N(0)_{vi}$  are the coincidence counting rates at  $\theta = 0$ , if all positrons annihilate in a perfect crystal region, at vacancy sites and vacancy-impurity pairs, respectively.

Snead et al. [23] studied the Al-1.7 at% Zn alloy using the positron lifetime technique. In their analysis they assumed  $A_v \mu_v = A_{vi} \mu_{vi}$  and obtained the binding energy between a vacancy and a zinc atom to be  $0.019 \pm 0.004$  eV or  $B_{vZn}$  (in Al)  $< 0.04$  eV.

Doyama et al. [24] measured the change in the peak counting rate in Cu-Al and obtained the binding energy between a vacancy and an aluminum atom to

be  $0.15 \pm 0.10$  eV. Doyama et al. [15] (fig. 3) analyzed the data on Cu-0.5 at% Ge by the most probable method by Powell [26] and obtained  $E_V^F = 1.28 \pm 0.10$  eV,  $B_{vGe} = 0.27 \pm 0.10$  eV,  $N(0)_v = 1.103 \pm 0.005$ ,  $N(0)_{vGe} = 1.091 \pm 0.005$ ,

$$A_v \mu_v / \lambda_f = \left( 9.1 \begin{smallmatrix} +5.0 \\ -3.0 \end{smallmatrix} \right) \times 10^5$$

and

$$A_{vGe} \mu_{vGe} / \lambda_f = \left( 8.6 \begin{smallmatrix} +5.0 \\ -3.0 \end{smallmatrix} \right) \times 10^5.$$

The author feels that the formation energy of a vacancy in copper in this analysis is rather high. Fixing  $E_V^F = 1.23$  eV,  $B_{vGe}$  becomes  $0.20 \pm 0.10$  eV. Triftshäuser and Jank [27] obtained  $B_{vMg}$  (in Al) =  $0.12 \pm 0.03$  eV and  $B_{vGe}$  (in Cu) =  $0.23 \pm 0.10$  eV, but found a repulsive interaction between a vacancy and silver in gold.

### 5.3. Quenching experiments

A large number of quenching experiments for the determination of the binding energy between a vacancy and a substitutional atom,  $B_{vi}$ , in dilute aluminum alloys were published in the 1960s. The principle is as follows. A dilute alloy is quenched and the increase in residual electrical resistivity  $\Delta\rho$  due to quenching is measured as a function of quenching temperature  $T_q$ . Here  $\Delta\rho$  is proportional to the concentration of vacancies. Plotting the logarithm of  $\Delta\rho$  against  $1/T_q$ , the apparent formation energy  $E_V^F(T)$  in eq. (5) is obtained. From this the binding energy  $B_{vi}$  can be estimated. The results before about 1970 indicated high binding energies. Some of the results can be found in refs. [1-4] and [9]. The impurity diffusion experiments in dilute aluminum alloys suggested the binding energy to be rather small. In those days the formation energy of a vacancy in pure aluminum was believed to be 0.76 eV based upon Simmons and Balluffi's experiment. The binding energy is quite sensitive to the difference between the formation energy of a vacancy and the apparent formation energy of a vacancy. A small shift in the formation energy of a vacancy introduces a large shift in the binding energy. At present the best value is believed to be 0.70 eV [28]. This appreciably lowers the binding energy. Another criticism of this experiment is the change during quenching.

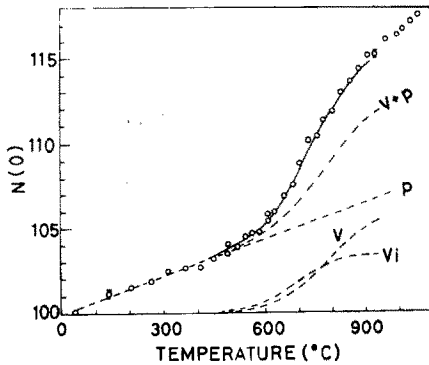


Fig. 3. The coincidence counts for the case of two annihilation gamma-rays emitted in opposite directions,  $N(0)$ , are plotted against temperature. P denotes the contribution to  $N(0)$  from positrons annihilating in a perfect region, V at vacancies and Vi at vacancy-impurity pairs.  $N(0)$  is normalized to the room temperature measurements.

Impurity clusters are formed during quenching. In recent experiments very dilute alloy specimens are used. The difference in the contribution to the electrical resistivity between a free vacancy and a vacancy-impurity atom pair and between a single impurity and a cluster of impurity atoms per impurity atom has not been included. Takamura [29] tried to associate all the vacancies with impurity atoms by aging for a short time. He called this state the "all bound" state. However, some solute clustering occurs during this process. Takamura's group obtained  $B_{\text{vZn}}$  (in Al) =  $0.02 \pm 0.02$  eV [30],  $B_{\text{vSi}}$  (in Al) =  $0.07 \pm 0.02$  eV [31],  $B_{\text{vMg}}$  =  $0.04 \pm 0.01$  eV [32],  $S_{\text{vZn}}$  (in Al) =  $-(4.0 \pm 1.2) k$  [30],  $S_{\text{vSi}}$  (in Al) =  $-(1.7 \pm 0.5) k$  [31] and  $S_{\text{vMg}}$  (in Al) =  $-(2.7 \pm 0.2) k$  [32]. If one plots the binding energy against the Debye temperature of the pure solute one obtains a linear relationship.

#### 5.4. Aging experiments

Kimura and Hasiguti [33,34] assumed that the rate of formation of G.P. zones is proportional to the total fractional concentration of vacancies. A number of aging experiments have been performed to estimate the binding energy  $B_{\text{vi}}$ . This is one of the most important metallurgical problems and it is definite that the binding energy  $B_{\text{vi}}$  plays an important role in the process. Usually the initial rate of aging is assumed to be proportional to the total fractional concentration of quenched-in vacancies. However, this is a rather complicated process and it is difficult to measure the binding energy  $B_{\text{vi}}$  quantitatively because of the vacancy and solute clustering.

In another experiment the total fractional concentrations of vacancies are measured from the size and density of dislocation loops formed by aging after quenching. From this the binding energy  $B_{\text{vi}}$  is estimated [35]. However, when the binding energy is low it is not easy to determine the difference in the total concentration in the pure matrix metal and dilute alloys. It should be remembered also that one can only see dislocation loops larger than the resolution of an electron microscope.

#### 5.5. Impurity diffusion experiments at high temperatures

Substitutional impurities in fcc metals diffuse by the vacancy mechanism. Consider here the "five-frequency model".

The self-diffusion coefficient is given by [36]

$$D_0 = A_0 \exp(-E_0^{\text{D}}/kT). \quad (23)$$

The impurity diffusion coefficient is given by

$$D_2 = A_2 \exp(-E_2^{\text{D}}/kT), \quad (24)$$

by the vacancy mechanism

$$E_0^{\text{D}} = E_{\text{V}}^{\text{F}} + E_{\text{V}}^{\text{M}}, \quad (25)$$

$$E_2^{\text{D}} = E_2^{\text{F}} + E_2^{\text{M}} - C, \quad (26)$$

and

$$\frac{A_2}{A_0} = \frac{\nu_2 f_2}{\nu_0 f_0} \exp\left(-\frac{C}{kT}\right),$$

where  $f_0$  and  $f_2$  are the correlation factors for self-diffusion and impurity diffusion, and

$$C = k \frac{\partial \ln f_2}{\partial (1/T)}, \quad (27)$$

in which

$$f_2 = (w_1 + \frac{7}{2}Fw_3)/(w_1 + w_2 + \frac{7}{2}Fw_3). \quad (28)$$

Here the usually accepted notation is used. The difference in the activation energies between impurity and self-diffusion  $\Delta E^{\text{D}}$  can be written as

$$\begin{aligned} \Delta E^{\text{D}} &= E_2^{\text{D}} - E_0^{\text{D}} = (E_2^{\text{F}} - E_{\text{V}}^{\text{F}}) + (E_2^{\text{M}} - E_{\text{V}}^{\text{M}}) - C = B_{\text{vi}} \\ &+ \Delta E_2^{\text{M}} - C. \end{aligned} \quad (29)$$

The impurity diffusion experiments on dilute aluminum alloys by Peterson and Rothman [37] and by Alexander and Slifkin [38,39] show that the values of  $\Delta E^{\text{D}}$  for many impurities are low. This indicates that the binding energy between a vacancy and an impurity in aluminum is small. Impurity diffusion in silver and copper has been widely investigated. [40,41] In these alloys the correlation between the activation energy of impurity diffusion and the position of the impurity in the periodic table is clear.

#### 5.6. Other experiments

The Mössbauer technique has been applied to this problem by Sørensen and Cotterill [42]. Specimens

Table 2  
Some experimental values of the binding energy  $B_{Vi}$  (in eV)

Solvent	Solute	Valency	$B_{Vi}$	$S_{Vi}^b/k$	Method	Ref.
Al	Cu	1	$0.00 \pm 0.12$	$0.0 \pm 1.5$		20, 4
	Ag	1	0.05	-0.5		17, 4
	Ag	1	0.013			63
	Mg	2	$-0.01 \pm 0.04$	$-0.1 \pm 0.5$		18, 4
	Mg	2	$0.04 \pm 0.01$	$2.7 \pm 0.2$	Q	32
	Zn	2	0.019		PA	23
	Zn	2	0.02	$-4.0 \pm 1.2$	Q	30
	Zn	2	0.10		Q	64
	Si	4	0.07	$-1.7 \pm 0.5$	Q	31
	Si	4	0.03	-2.0		19, 4
Cu	Al	3	$0.15 \pm 0.10$		PA	24
	Ge	4	$0.27 \pm 0.10$		PA	25
	Ge	4	$0.25 \pm 0.10$		PA	27

of high purity aluminum, doped with Mössbauer impurities of either  $^{119}\text{Sn}$ ,  $^{57}\text{Fe}$ , or  $^{57}\text{Co}$  were quenched and annealed. They observed the clustering of impurity atoms even in very dilute alloys. The estimated binding energy  $B_{V\text{Sn}}$  (in Al) is less than 0.3 eV (table 2).

## 6. Calculations of the binding energy $B_{Vi}$

The interaction between a vacancy and a substitutional impurity atom should be able to be treated by a self-consistent electronic theory, but is normally separately treated by elastic theory and electronic theory.

### 6.1. Elastic theory

It is probably inappropriate to extend the macroscopic elastic theory to an atomic scale. However, some attempts have been made. Overhauser [43] and Swalin [44] paid attention to the difference in the sizes and bulk moduli of solvent and solute atoms. Friedel [45] calculated the heat of solution  $H_s$  as

$$H_s = \frac{6\pi(r_i - r_s)^3 r_i B_i N}{1 + (2B_i r_i / B_s r_s)}, \quad (30)$$

where  $N$  is the Avogadro number,  $r_i$  and  $r_s$  are the radii of an impurity and a matrix atom,  $B_i$  and  $B_s$  are the bulk moduli of impurity and matrix atoms. Swalin as-

sumed that  $B_{Vi}$  is  $H_s/Z$ , where  $Z$  is the coordination number.

### 6.2. Screening potential method

Lazarus [46] applied the concept of a screening potential to the difference in the valence electrons of solute and solvent atoms. The binding energy is given by

$$B_{Vi} = \Delta Z e V(d) = -\frac{\Delta Z e^2 \alpha}{d} \exp(-\lambda d), \quad (31)$$

where  $\Delta Z$  is the difference in the valency of the solvent and solute,  $e$  is the electron charge,  $V(d)$  is the solute potential at a nearest neighbor site,  $d$  is the nearest neighbor distance, and  $\alpha$  and  $\lambda$  are constants. This theory has also been developed by LeClaire [48] and many authors [47]. The numerical results are shown in table 3.

The screening potential method is unsatisfactory for the following reasons. The impurity atoms are only characterized by the difference in the valence of the impurity and that of the matrix atoms. Vacancy-impurity interaction energies vanish for the impurity atoms whose valence is the same as that of the matrix atoms. The electronic structure of the conduction electrons in metals is not appropriately included. Oscillatory behavior has not been taken into account. March and Rousseau [2] reviewed this problem.



Table 3

Calculated values of the binding energy  $B_{vi}$  (in eV)

Method	$\Delta Z$	T.F.	T.F.	T.F.	Oscillatory
Solvent		Cu	Ag, Au	Al	
Solute	+4	-0.123	-0.077		
	+3	-0.101	-0.063		
	+2	-0.075	-0.047	-0.091(Sb)	0.013(Sb)
	+1	-0.043	-0.028	-0.046(Ge)	0.0065(Ge)
	-1	+0.078	+0.055	+0.046(Zn)	-0.0065(Zn)
	-2	+0.207	+0.151	+0.091(Cu)	-0.013(Ag)
	-3	+0.391	+0.294		
Ref.		53	53	37	37

### 6.3. The pseudopotential and oscillatory potential methods

Many properties have been successfully calculated by the pseudopotential method. The interaction between a vacancy and an impurity atom has been calculated [49–52] within the framework of the pseudopotential method based on second-order perturbation theory.

The vacancy-impurity interaction can be written as

$$\phi_{vi}(R) = -\frac{Z_M \Delta Z_i e^2}{R} + \frac{\Omega_M}{\pi^2} \times \int_0^\infty q^2 \frac{\sin qR}{qR} [F_{MM}(q) - F_{Mi}(q)] dq, \quad (31)$$

where the subscripts M and i denote matrix and impurity,  $R$  is the distance between a vacancy and an impurity atom,  $\Delta Z_i = Z_i - Z_M$ ,  $F_{\alpha\beta}(q)$  is the energy-wave-number characteristic defined by

$$F_{\alpha\beta}(q) = \omega_\alpha(q) \omega_\beta(q) \chi_M(q) \epsilon_M(q), \quad (32)$$

where  $\omega_\alpha(q)$  and  $\omega_\beta(q)$  are the form factor of atom  $\alpha$  and atom  $\beta$ , respectively.  $\chi_M(q)$  and  $\epsilon_M(q)$  are the perturbation characteristic and the dielectric function of the matrix metal given by

$$\chi_M(q) = -\frac{1}{2} Z_M \left( \frac{2}{3} E_F^M \right)^{-1} \left( \frac{1}{2} + \frac{4(k_F^M)^2 - q^2}{8qk_F^M} \ln \left| \frac{q + 2k_F^M}{q - 2k_F^M} \right| \right) \quad (33)$$

and

$$\epsilon_M(q) = 1 - \frac{8\pi e^2}{\Omega_M q^2} [1 - f(q)] \chi_M(q), \quad (34)$$

where  $f(q)$  is the correlation factor for exchange and correlation effects of the conduction electrons.  $E_F^M$  and  $k_F^M$  are the Fermi energy and Fermi wave number of the matrix. The first term of eq. (31) is the direct Coulomb interaction between the excess charges of point defects; the second is the indirect interaction

Table 4

Vacancy-impurity binding energies  $B_{vi}$  at nearest neighbor positions in aluminum (in eV) [52]

Impurity	Z	Correlation HS	factors (q) SSTL
Li	1	0.045	0.020
Na	1	0.083	0.034
K	1	0.192	0.123
Rb	1	0.195	0.127
Cs	1	0.211	0.141
Cu	1	0.045	0.027
Ag	1	0.045	0.020
Au	1	0.045	0.027
Mg	2	0.042	0.009
Zn	2	0.031	0.007
Hg	2	0.020	0.019
In	3	0.018	-0.004
Sn	4	-0.003	-0.015
Pb	4	0.038	-0.001
Bi	5	0.038	-0.004

due to the screening by conduction electrons in a metal.

Takai et al. [52] used the empty core model potential of Ashcroft [54]. The correlation function  $f(q)$  in eq. (34) has been extensively studied by many authors. Takai et al. [52] used the random-phase approximation [53] (referred to as RPA), the Hubbard-Sham approximation [55,56] (referred to as HS) and the Singwi, Sjolander, Tosi and Land approximation [57] (referred to as SSTL). Table 4 shows the results of  $B_{vi}$  (in Al) calculated by Takai et al. [52].

Takai et al. [54] found the following relationships between the calculated vacancy-impurity binding energy and the core radius  $R_c$ , The Debye temperature  $\Theta_D$  and the melting temperature  $T_m$  in an aluminum matrix.

$$B_{vi} = 0.027[(R_c^i)^3 - (R_c^M)^3]/(R_c^M)^3 \quad (\text{eV}), \quad (35)$$

$$= 8.8[(\Theta_D^i)^{-1} - (\Theta_D^M)^{-1}] \quad (\text{eV}), \quad (36)$$

$$= 7.0 |(T_m^i)^{-1/2} - (T_m^M)^{-1/2}| \quad (\text{eV}). \quad (37)$$

Superscripts M and i denote matrix and impurity, respectively.

#### 6.4. Other calculations

Extending the Anderson model of localized magnetic states in metals, Masuda [59] calculated the binding energy  $B_{vi}$  between a vacancy and a transition metal impurity in copper to be  $-0.192 \text{ eV} < B_{vi} < 0.338 \text{ eV}$  from Ti to Ni.

### 7. Empirical relations

A few empirical relations have been proposed. Hasi-guti [60] proposed the binding energy between a vacancy and a substitutional atom  $B_{vi}$  as a function of the difference in the valence and size of solute atoms as

$$B_{vi} = E_0 + E_z \Delta Z + \left( \frac{d - d_0}{d_0} \right) E_s, \quad (38)$$

where  $E_0$ ,  $E_z$  and  $E_s$  are constants,  $d_0$  and  $d$  are the atomic diameters of solvent and solute atoms, and  $\Delta Z$  is the difference in valence between solvent and solute.

Doyama [9] proposed a relation between the solubility limit  $c_L$  of the solute atoms in the solvent and

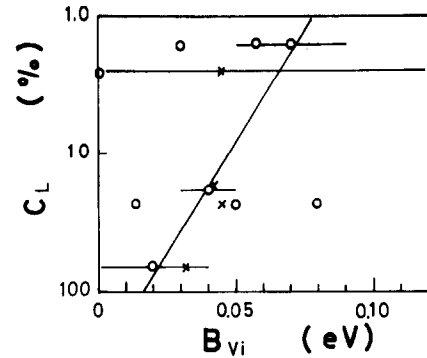


Fig. 4. A relation between the vacancy-impurity binding energy  $B_{vi}$  in aluminum and the impurity solid solubility  $c_L$  in aluminum. Crosses are the values calculated by the HS approximation.

suggested

$$B_{vi} = -A \log c_L + B. \quad (39)$$

The solubility at temperature  $T$  can be expressed by the heat of solution (fig. 4),  $H^s$ , as

$$\frac{c_s}{1 - c_s} = A \exp \left( - \frac{H^s(1 - 2c_s)}{kT} \right). \quad (40)$$

Then the binding energy between a vacancy and an impurity atom is proportional to the heat of solution (fig. 5), i.e.

$$B_{vi} = \alpha H^s. \quad (41)$$

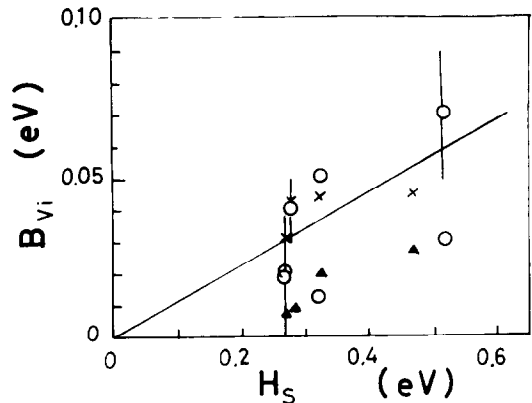


Fig. 5. A proportional relationship between the vacancy-impurity binding energy  $B_{vi}$  and heat of solution  $H_s$ . The straight line shown is for  $B_{vi} = H_s/9$ . Crosses indicate values calculated by the Hubbard and Sham approximation and triangles indicate the SSTL approximation.

It is easy to understand the relationship between the solubility limit, heat of solution, and the binding energy  $B_{vi}$ . If the energy required to replace a solute atom with an impurity atom, that is, the heat of solution, is high, the solubility limit is low; and also the distortion (lattice and electronic) near the impurity atom is high. When a vacancy is trapped next to the impurity atom, this distortion is relaxed. The relaxation energy, that is the binding energy, is higher as the distortion is larger.

Swalin [44] assumed that one-twelfth of the distortion is released when a vacancy comes next to a solute atom. Therefore according to his concept  $\alpha$  in eq. (41) is  $\frac{1}{12}$ .

Seeger [61] suggested that the binding energy can be written using the nearest neighbor bond as

$$B_{vi} = (H_{\text{coh}}^A - H_{\text{coh}}^B - H^s)/Z, \quad (42)$$

where  $H_{\text{coh}}^A$ ,  $H_{\text{coh}}^B$  and  $H^s$  are the cohesive energies of pure A and pure B, and the heat of solution of the solution atoms. He obtained 0.15, 0.17 and 0.05 eV for Al-Mg, Al-Zn, and Al-Ag alloys. Eq. (42) means that if the configurational energy of an AB binary alloy  $H$  is plotted against the fractional concentration  $x$  of the B component, and the derivative with respect to  $x$  is taken then

$$B_{vi} = -\frac{1}{Z} \frac{\partial H}{\partial x}. \quad (43)$$

Doyama and Koehler [62] suggested that the bond between a vacancy and an atom is not zero. They called this bond a "ghost bond" and showed that

$$E_{AV} = 0.7 E_{\text{coh}}/Z \quad (44)$$

for many pure metals. Then Seeger's relation has to be modified as

$$B_{vi} = -E_{AB} + E_{BV} - E_{AV} + E_{AA} = \{0.3[E_{\text{coh}}^A - E_{\text{coh}}^B(C_B = 0)] - H^s\}/Z. \quad (45)$$

It should be noted that in eqs. (42) and (44)  $E_{\text{coh}}^B$  is not the cohesive energy of B but not that of B atoms  $E_{BB}$  in pure A ( $C_B = 0$ ,  $C_A = 1$ ).

## 8. Conclusions

(1) The difference between the formation energy of a vacancy in a pure matrix and the apparent forma-

tion energy of a vacancy in a dilute alloy is presented. A slight shift in the formation energy of a vacancy in the pure matrix appreciably affects the determination of the binding energy of a vacancy-solute pair. Particularly for the case of a low binding energy the experiments are difficult.

(2) Simultaneous measurement of the changes in the macroscopic length and lattice parameter is a good technique but the sensitivity of the experiment, and the dispersion and clustering of solute atoms are some of the problems.

(3) Positron annihilation is quite sensitive and a new tool to determine the binding energy. It should be noted this is not a linear quantity with the concentration of vacancies.

(4) Impurity diffusion experiments give information about  $B_{vi}$ , but not very directly.

(5) Quenching experiments always have problems due to changes during quenching.

(6) Theory on  $B_{vi}$  has been developed quite rapidly, but the quantitative numerical results should not be taken very seriously.

In conclusion very few convincing experimental and theoretical values are available at present.

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