A stochastic theory for clustering of quenched-in vacancies— 2. A solvable model

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Abstract. The model introduced for clustering of quenched-in vacancies in the first part of this series of papers is considered. Using a generating function, the rate equations are converted into a first order partial differential equation for the generating function coupled to a differential equation for the rate of change of the concentration of single vacancy units. A decoupling scheme is effected which gives an exponentially decaying solution with a very short time constant for the concentration of single vacancy units. The differential equation for the generating function is solved for times larger than the time required for the concentration of single vacancy units to reach its asymptotic value. The distribution for the size of the clusters is obtained by inverting the solution thus obtained. Several results that follow are shown to be in reasonably good agreement with the experimental results.

1. Introduction

In the previous paper (Ananthakrishna 1979a, referred to as paper I hereafter), we introduced a model which can be solved in closed form. This model specialises to a situation where the total number of vacancies in the cluster is quadratic in the linear dimension of the cluster. This corresponds to the formation of stacking fault tetrahedra and vacancy loops. The approach of this model consists in writing down a system of n-coupled rate equations (the differential-difference equations) for the growth of clusters assuming that only single vacancy units are mobile. The general rate equation given by equations (2), (3) and (4) of paper I cannot be solved even on a computer when the number of such equations exceed about 10^3. It is for this reason that Kiritani (1973) resorts to a grouping method (which in essence is coarse graining). The resulting equations are then solved on a computer. Thus the evolution of clusters cannot be followed in a precise way when the number of equations is large. The grouping operation itself has been criticised by Kiowa (1974) based on comparison of results of a solvable model (Montroll 1967) with the numerical results obtained on a computer using the grouping operation. Hayns (1976) has studied the effect of the grouping operation and finds that it yields consistent results when handled carefully. He also observes that the grouping method is the only method that offers hope of obtaining solutions to problems where such large number of coupled equation are involved in the absence of any analytic method. Thus it is desirable to evolve a solvable method which preserves the essential features of the physical system and which can be solved in closed form. The model that we have

introduced in paper I is a first step in this direction and will form the basis for further work presented in papers III and IV (Ananthakrishna 1979b and 1979c). Although the model gives a rather peaked distribution possibly due to the choice of the number of absorption and emission sites, and the assumption of constant binding energy, some comparison is possible with experiments. We shall discuss the advantages, disadvantages, possible reasons for the drawbacks and how these inadequacies will be overcome in subsequent papers. In the present paper we deal with the solution of this model in detail as this model will serve as a starting point for a continuum model (paper III, Ananthakrishna 1979c, Ananthakrishna 1977). We shall first recall the major idealizations in this model. We shall try to give some justification for these assumptions.

The rate equations have been written down by assuming the growth of clusters proceeds via the absorption and emission of single mobile units. (In the case of gold and aluminium, divacancies are considered as the mobile units.) This assumption is justified in most cases, particularly for the cases considered namely for aluminium and gold. For instance, the mobility of the monovacancies are two to three orders of magnitude smaller than that of divacancies at temperatures of interest and the other clusters are practically immobile (Kiritani 1973). Further the results of computer calculations of Kiritani (1973) with one mobile unit compare well with experiments thus offering a justification for this assumption. It is expected that the next mobile species may become important only at late stages of clustering. We have also considered the system to have no sinks. This assumption is not serious since as far as the phenomenon of clustering is concerned, only supersaturation of vacancies is required. So ignoring sinks would effectively increase the supersaturation and would thus aid clustering. This in turn may lead to increased concentration of clusters. The support for this claim can again be had from the computer calculations of Kiritani (1973). His work demonstrates that a system without sinks is sufficient to describe the phenomenon of clustering. Now if we wish to solve these equations in closed form further assumptions have to be made. This involves assuming that the binding energy of a vacancy unit in a cluster is independent of the size of the cluster as far as the growth of clusters is concerned. The justification for this assumption is three-fold. First, the binding energy for vacancy loops and stacking fault tetrahedra saturates very rapidly, reaching a near asymptotic value for $n = n_s \sim 250$, whereas the number of vacancies in a cluster of average size is of the order of 10^5, which suggests that the assumption is justified. In view of this, the emission rate depends on $\langle n \rangle$ as we will show later, where $\langle \ \rangle$ is taken over the distribution N_n. In table 1, we have given the variation of b_n as a function of n for aluminium. The binding energy changes rapidly only for $n \leqslant 50$. Thus the variation of b_n as a function of n, can be seen to be small for the region of interest. Second, by taking the same binding energy for all clusters, we will be essentially overestimating the density of small clusters. This can be seen from the binding energy curve (Kiritani 1973 and table 1) which suggests that the probability of emission from smaller clusters is larger than that from larger clusters. Third, and probably the best in our view, with this assumption the equations are mathematically tractable in closed form. Further, the emission probability, as will be shown later, will be related to experimentally measurable quantities and therefore can be regarded as a parameter to be fixed by comparison with experiments. Thus x_2 which was originally a function of n has been regarded as a function of $\langle n \rangle$. (For this reason, this factor takes into

Table 1. Binding energy b_n as a function of n for aluminium.

n	b_n (eV)	$\exp\left[-b_n/kT\right]$; $T=230°K$
10	0·303	$1·14 \times 10^{-6}$
20	0·357	$3·75 \times 10^{-7}$
30	0·382	$1·33 \times 10^{-7}$
40	0·398	$6·85 \times 10^{-7}$
50	0·407	$4·72 \times 10^{-8}$
100	0·437	$1·36 \times 10^{-8}$
150	0·450	$7·94 \times 10^{-9}$
200	0·458	$5·70 \times 10^{-9}$
300	0·470	$3·46 \times 10^{-9}$
400	0·481	$2·19 \times 10^{-9}$

account and corrects for the various idealisations in the theory. See § 4.) Once this assumption is made, these equations can be solved using a generating function.

The problem we wish to solve is: given that initially we have a supersaturated system of vacancy units with a concentration N_1, could we predict the distribution of $N_n(t)$ at any instant of time t? Our main aim would only be the statistical aspects of clustering. Given the transition probabilities for the association and dissociation, we would only be interested in obtaining the distribution function $N_n(t)$. The details and the precise mechanisms by which a particular type of defect aggregate is formed will not be relevant. (For example the growth of tetrahedra may be due to the movement of vacancy ledges). However, the energies associated with these mechanisms of formation of the defect aggregates would enter into the transition probabilities. Making use of the method of generating function we obtain a partial differential equation for the generating function coupled to a differential equation for rate of change of the concentration of single vacancy units. Although we are not interested in short time aspects of clustering, we do obtain some information about the nucleation times via the solution of the concentration of single vacancy units which has already been outlined in paper I and will not be repeated here. The basic idea involved is to decouple the differential equation governing the rate of decay of the concentration of single vacancy units from that of the differential equation for the generating function in an appropriate way. This is possible because the total number of vacancies in the system is conserved. As we have seen this yields (paper I) an exponentially decaying solution for the concentration of single vacancy units with a small time constant, which means that the concentration of single vacancy units attains an equilibrium with the configuration of small clusters in a very short time. Then using the asymptotic value of the concentration of single vacancy units, the solution of the equation for the generating function is obtained. By inverting this solution we obtain the distribution function for the cluster sizes. The results of the average quantities that follows are in reasonably good agreement with the experimental results on the formation of stacking-fault tetrahedra in quenched gold (Jain and Siegel 1972a), and the formation of faulted vacancy loops in quenched aluminium (Kiritani 1973; Yoshida *et al* 1963).

2. Solution of the model

We shall briefly summarise a few results on the formation of stacking fault tetrahedra and faulted vacancy loops in quenched gold and aluminium respectively. Stacking fault tetrahedra are formed in quenched gold with their four stacking-fault sides on the four non-parallel $\{111\}$ planes arranged in a tetrahedral shape. The edges of the tetrahedran are parallel to the six $\langle 110\rangle$ directions. In the case of aluminium, the loops formed are hexagonal and are formed on the $\{111\}$ planes bounded by $\langle 110\rangle$ directions. As much as 95% of the vacancy loops formed are faulted under certain conditions (Kiritani *et al* 1964). Other types of extended defects which are formed will not be considered in this work. (However, the theory holds for all planar configurations and stacking-fault tetrahedra.) For simplicity we shall assume that the tetrahedra are regular and the loops circular. We shall use the total number of vacancies contained in the cluster to be L^2/a^2 or $4\pi\, r^2/a^2\sqrt{3}$, where a is the lattice constant, L the edge length of the tetrahedra and r the radius of the loop. The energy of formation of such tetrahedra and loops as a function of the number of vacancies contained in the cluster is given by (Cotterill 1965).

$$\epsilon_n = A_i\, n + B_i\, n^{1/2}\ln\,(c_i\, n);\ i = L, T, \tag{1}$$

with
$$A_T = \gamma\, a^2\sqrt{3},\ A_L = \gamma\, a^2\,\sqrt{\tfrac{3}{4}},\ C_T = 8,\ C_L = \tfrac{2}{3},$$

$$B_T = Ga^3/[24\pi(1-v')]\ \text{and}$$

$$B_L = Ga^3/[4\pi\, 6^{1/2}\,(1-v')]$$

The subscripts refer to tetrahedra and loops respectively. (In the above expression, G is the shear modulus, v' the poissons ratio, and γ the stacking-fault energy). The binding energy is

$$b_n = E_V^F - [\epsilon_n - \epsilon_{n-1}],$$

which for large n takes the form

$$b_n \simeq E_V^F - A_i - B_i\, [2 + \ln c_i + \ln\,(n-1)]/2n^{1/2}. \tag{2}$$

This formula has been obtained by using

$$(n-1)^{1/2} \simeq n^{1/2} - n^{-1/2}/2 \text{ and } \ln\,[1 - (1/n)] \simeq 1/n.$$

Therefore (2) approximates the exact one for $n \gg 1$. (Indeed, it agrees reasonably well for $n \geqslant 100$). This above equation tells us that b_n is a slowly varying function of n for large n. An exact calculation indicates that b_n saturates very rapidly reaching the asymptotic value for $n \sim 200$. (See for example Kiritani 1973.)

The concentration of single vacancies between the usual quenching and the ageing temperatures differs by ten orders of magnitude. This excess of vacancy concentration leads to the formation of clusters of finite size via the collision of single mobile units. We shall also assume that the quenching is instantaneous and nearly 50%

of the single vacancies are in the form of divacancies before the sample temperature reaches that of the temperature of the bath. In cases where there is some uncertainty in the concentration of vacancies stored in the clusters, we have estimated it by using the average size and density (as we have done in the case of the data given by Kiritani 1973, for aluminium).

The rate equations have been written down in the earlier paper (paper I). We shall refer the equations in paper I by (I.n.). In the following we shall show that x_2 in this picture should be regarded as a function of $\langle n \rangle$ instead of n. This is a consequence of our assumption about the constancy of the binding energy. From (2) it is clear that the term $n^{-1/2} \ln (n-1)^{1/2}$ is the slower term of the two. Using this fact and $\psi(n) = n-1$ and $\bar{\psi}(n) = n$ in the equation for N_1, we have

$$-\frac{dN_1}{dt} = x_1 N_1^2 + x_1 N_1 \sum_2 n N_n - \sum_2 n x_1 x_2(n) N_n.$$

This can be written as

$$-\frac{dN_1}{dt} = x_1 N_1^2 + x_1 N_1 f(t) - x_1 x_2 (\langle n \rangle) f(t).$$

If b_n rapidly saturates as we have pointed out namely for $n \sim 200$. This is permissible under the condition that $x_2(n)$ is a rapidly saturating function whereas the peak of the distribution occurs in experimental situations at a very large values. (see table 2). Strictly

$$\sum_2 n x_2(n) N_n = \langle n x_2(n) \rangle \bar{N},$$

where $\bar{N} = \sum_2 N_n$. Now if we use

$$\langle x_2(n) n \rangle \simeq \langle n \rangle \langle x_2(n) \rangle \simeq \langle n \rangle x_2(\langle n \rangle),$$

we get the result indicated above. This is somewhat the mathematical equivalent of the assumption about constant binding energy. We shall later show that this is what follows in the final analysis. In fact, here it would have been sufficient to have taken x_2 as a constant. This approximation does not affect N_1 and the average values much, but affects the distribution. We remedy this problem in the next paper (paper

Table 2. The values of the parameters used

	E_v^F (eV)	E_v^M (eV)	E_{vv}^M (eV)	S/k	ν in sec^{-1}	Z_1	Z_2
Au	0·94	0·86	0·55	1·0	3×10^{13}	10	10
Al	0·76	0·56	0·46	2·4	3×10^{13}	10	10

III).   The validity of these two statements can be seen by the fact that both dN_1/dt and df/dt depend on

$$\sum_2 x_2\,(n)\,nN_n$$

which we have approximated by $x_2\,(\langle n\rangle)\,f(t)$ and thus the effect on N_1 should be less in contrast to the effect on N_n which depends on $x_2\,(n)$ approximated by $x_2\,(\langle n\rangle)$. It is worthwhile commenting on the choice of $\psi\,(n)$ and $\bar{\psi}\,(n)$. This choice has been made since it is the only choice that allows the decoupling of equations (I.3) and (I.4) from (I.2) even with the assumption that x_2 is independent of n. We shall demonstrate this point shortly. Before that some observations can be made about ψ and $\bar{\psi}$. These factors correspond to the number of absorption and emission sites respectively. In a real physical situation the number of emission and absorption sites are functions of the size of the cluster. For example, in the case of a vacancy loop the number of absorption and emission sites which depend linearly on n for small n can be expected to reach an asymptotic value of $n^{1/2}$ for large loops. Nevertheless, for simplicity we shall use the above relation to hold in our model. This may be one of the factors which is responsible for the unphysical nature of the distribution. We shall comment more on this later. Rewriting equations (I.2), (I.3) and (I.4) using (I.17) and (I.18) we have,

$$\frac{dN_1}{dt} = -x_1\,N_1^2 + x_1\,[x_2\,(\langle n\rangle) - N_1]\,f(t), \tag{3}$$

$$\frac{dN_2}{dt} = \tfrac{1}{2}\,x_1\,N_1^2 - x_1\,x_2\,(\langle n\rangle)\,N_2 + 3\,x_1\,x_2\,(\langle n\rangle)\,N_3 - 2\,x_1\,N_1\,N_2, \tag{4}$$

and $$\frac{dN_n}{dt} = (n-1)\,x_1\,N_1\,N_{n-1} + (n+1)\,x_1\,x_2\,(\langle n\rangle)\,N_{n+1}$$

$$- n\,x_1\,N_1\,N_n - n\,x_1\,x_2\,(\langle n\rangle)\,N_n. \tag{5}$$

Since $$f(t) = \sum_2 n\,N_n = N_0 - N_1, \tag{6}$$

equation (3) is entirely a function of N_1 and thus leads to an exact solution of N_1. We can now show that we cannot decouple the equation for N_1 from that for N_n unless ψ and $\bar{\psi}$ are chosen to be $(n-1)$ and n respectively. It is clear that any deviation from linearity like $\psi(n) \sim n^{1/2}$ or any power of n leads to a hierarchy of equation in functions

$$f(t),\, f_1(t) = \sum \psi(n)\,N_2,\, f_2(t) = \sum N_n\,\psi^2\,(n),\ \text{etc.}$$

Thus the decoupling of the equation is not possible. Even a slightly different choice

of ψ and $\bar{\psi}$ (preserving the linearity in n) would also disallow such a decoupling. Consider using

$$\psi(n) \to \psi(n) + a,$$

and

$$\bar{\psi}(n) \to \bar{\psi}(n) + b.$$

Then

$$-\frac{dN_1}{dt} = (a+x_1) N_1^2 + x_1 N_1 f(t) + a x_1 N_1 \sum_2 N_n$$

$$- x_1 x_2 f(t) - b x_1 x_2 \sum_2' N_n.$$

This equation cannot be solved unless $\bar{N} = \Sigma_2 N_n$ is known. The factor $\bar{N}$ is a strong function of time for short times. This can be seen by the following argument. For short times after quenching, the rate at which the single vacancies are depleted is the cause for the production of small clusters. Also from the analysis when a and b are zero we know that N_1 has a very short time constant. Since $f(t)$ is linear in N_1 and $\bar{N} = f(t)/\langle n \rangle$, $\bar{N}$ would nearly have the same dependence as N_1 because in this short time $\langle n \rangle$ does not change much.

The solution of (3) has already been given. (see equation (I.19)). Here we shall discuss the result. It is clear that the asymptotic value of N_1 is $N_0 x_2/(N_0 + x_2)$. This expression, apart from giving the time dependence of N_1, also provides an estimate of the nucleation time of small clusters. If we regard the nucleation time as the time required to reduce the concentration of single vacancy units to approximately a few percent of the initial value, then the nucleation time for gold aged at 313°K and aluminium aged at 283°K is of the order of 10^{-2} sec. (The value of N_0 used is 3×10^{-4} and 2×10^{-4} respectively. These numbers have been obtained using the parameters listed in table 2. In the case of the formation of tetrahedra, the effective migration energy of divacancies decreases by 0·07 eV due to the temperature dependent sink efficiency of tetrahedra. See Jain and Siegel 1972b; Sahu *et al* 1976.) This result agrees with the computer calculations of Kiritani (1973) for the case of aluminium. The time constant is determined by the product of the mobility and the initial concentration of single vacancy units (since $x_2 \ll N_0$ as will be shown later). Thus the nucleation time rapidly increases as the temperature is reduced. (The above definition of the nucleation time has the simple interpretation that it is the time required for the formation of clusters of small sizes having a few vacancy units on an average.) The fact that the concentration of single vacancy units decreases rapidly with a small time constant coupled with (6) tells us that the concentration of single vacancy units attains an equilibrium with the configuration of small clusters in a very short time. Since N_1 is monotonically decreasing, we can decouple (5) and (4) from (3) and solve (5) and (4). This decoupling scheme is permissible because the decay time of N_1 is very small in contrast to the time scale involved for the formation of large clusters as will be shown later on. Here it would be sufficient to indicate it by the following physical argument. In the initial stages of clustering only small clusters are formed. In course of time some clusters grow at the expense of other clusters via a redistribution of single vacancy units among themselves.

In order to solve (4) and (5) we use the generating function approach. We define

$$\chi(Z, t) = \sum_{2} N_n Z^{-n}; \ |Z| \geqslant 1.$$
(7)

Clearly both

$$\chi(1, t) = \sum_{2} N_n \text{ and } -\frac{\partial \chi}{\partial z}\bigg|_{|Z|=1} = f(t)$$

exist, since we know that the latter represents the total number of vacancy units in clusters of all sizes. Therefore $\chi(Z, t)$ is an analytic function of Z for all $Z \geqslant 1$, and all its derivatives exist in that region. Now we wish to transform (5) and (4) into a differential equation for $\chi(Z, t)$. This is done by multiplying (4) by Z^{-2} and (5) by Z^{-n} and summing over n. After suitable manipulations we get

$$\frac{\partial \chi}{\partial t} = \frac{x_1 N_1^2 Z^{-2}}{2} + \frac{\partial \chi}{\partial Z}(Z-1)(N_1 - Zx_2)x_1 + x_2 x_1 N_2(Z^{-2} - 2Z^{-1}).$$
(8)

We can see that if we set $Z=1$, we get the equation for $f(t)$. Equation (8) is a first order partial differential equation. We have obtained the solution of this differential equation for regions of time after N_1 has reached its asymptotic value with the assumption that ignoring the term N_2 does not affect the solution very much. The method of obtaining the solution and the justification for the above assumption about ignoring the N_2 term has been outlined in appendix 1. The solution that we have obtained with the initial condition that $\chi(Z, 0) = 0$, which reflects the fact that there are no clusters of finite size at $t = 0$, is

$$\chi(Z, t) = \frac{a}{c}\left\{\frac{1+b}{b^2}\ln\left[\frac{Z(1-b)}{Z-b-\phi b(Z-1)}\right] + \frac{1}{(b-1)}\ln\phi - \frac{1}{bZ}\right.$$

$$\left. + \frac{\phi(Z-1)+b-Z}{b[b-Z+\phi b(Z-1)]},\right.$$
(9)

where $b = N_0/(N_0 + x_2)$; $c = x_1 x_2$ and $a = x_2 cb^2/2$.

In order to obtain N_n, we have to invert the above function, which involves performing the contour integral

$$\frac{1}{2\pi i}\oint Z^{n-1}\chi(Z, t)\,dZ.$$
(10)

Instead, we expand the left hand side of (9) in inverse power of Z and collect the coefficient of Z^{-n}. This gives

$$N^n(t) = \frac{ab^{n-2}(1-\phi)^n}{c(1-b\phi)^n}\left[\frac{1+b}{n} + \frac{\phi(b-1)^2}{(1-\phi)(1-b\phi)}\right].$$
(11)

As $t \to 0$, clearly $N_n = 0$, which means that there are no vacancy clusters of finite size at $t = 0$. As $t \to \infty$, N_n takes the form given by

$$N_n = \frac{a(1+b)b^n}{b^2cn} = \frac{a(1+b)}{b^2nc} \exp\left[n \ln b\right],\tag{12}$$

which is the stationary solution of (5). The distribution given by (11) and (12) are peaked at the origin and therefore is not a realistic distribution. The reason for the non-evolution of the peak and the peaked nature of the distribution can be many-fold, some of which have been mentioned in §1. We have investigated this problem in detail and the development of a continuous model presented in the next paper (paper III) is the result of this investigation. Here we mention a few points in this connection.

The basis for the continuum model is this discrete constant binding energy model. A Taylor series expansion for $p_{n\pm1}$ is used upto second order. The resulting partial differential equation is slightly modified to satisfy the conservation of the total number of vacancies. This equation looks very *similar* to a Fokker-Planck equation but should be only regarded as a differential equation for the distribution function for the sizes of the clusters. The method used in developing the continuum model sheds some light on the problem at hand.

It may be recalled that the choice of the number of absorption and emission sites have been chosen to be $\psi(n)=n-1$ and $\bar{\psi}(n)=n$ respectively. In a realistic situation these can vary as the clusters grow for instance from n for small loops to $n^{1/2}$ for large loops. Such a change in the choice of ψ and $\bar{\psi}$ can give rise to very different partial differential equation for the distribution of clusters. The solutions will be very different and the position of the peak will be at non-zero value of n. Even in the case of the choice we have made for $\psi(n)$ and $\bar{\psi}(n)$, if we make a small change, it produces a different distribution as we have shown in the next paper. (see paper III). Indeed the differential equation which we have evolved self-consistently corresponds to a change by a factor of $\frac{1}{2}$ for both $\psi(n)$ and $\bar{\psi}(n)$. Another factor which may have contributed is the assumption about constant binding energy.

In the discrete model, it is possible to make the peak of the distribution evolve in time by choosing $\psi(n)=|n-n_0-1|$ and $\bar{\psi}(n)=|n-n_0|$, where n_0 is the position of the peak at $t \to \infty$. The value of n_0 has to be supplied by experiments. The method of attack is exactly the same and will not be given here as it does not give any better insight into the problem except for the final result. The distribution obtained in this case is

$$N_n = \begin{cases} \dfrac{A\, N_0\, (n_0-1)\, (b^3-b^n)}{(n_0-n)\,(1-b)}\, x_2, & \text{for } n < n_0 \\[4mm] \dfrac{A\, N_0(n_0-1)\,(b^3-b^{n_0})\, b^{n-n_0}}{(n-n_0)}\, x_2, & \text{for } n > n_0, \end{cases}$$

where A is normalisation constant. Although the distribution is not strictly symmetric about n_0, a plot of N_n for typical values of N_0, x_2 and n_0 shows that it is nearly symmetric.

In view of all the above statements we regard n in (11) and (12) to be measured from the peak, or we can rewrite the distribution in the form

$$N_n = \frac{2x_2\,(2N_0 + x_2)}{(N_0 + x_2)}\ \frac{b^{|n - n_0|}}{|n - n_0|}.$$

(13)

The position of the peak n_0 should be supplied by experiments.

3. Comparison with experiments

Having obtained the distribution function, we can compare several results with experiments. These are: (a) the decay of the concentration of single vacancy units and the nucleation time of small clusters, (b) the total density of the clusters as a function of time and temperature, (c) the average size of the clusters as a function of time and temperature, (d) the characteristic time for the growth of large clusters. We shall compare these quantities with the results on quenched gold and aluminium. (Kiritani 1973; Yoshida *et al* 1963; Jain and Siegel 1972a).

The first main result that emerges out of our theory is that the concentration of single vacancy units decreases exponentially with a very short time constant. This indirectly leads to information about the nucleation time. In a realistic situation, a cluster that becomes stable at some size may be regarded as a nucleus. In the case of vacancy loops, it has been experimentally well established that there is no stable cluster and the binding energy increases gradually with size (Kiritani *et al* 1969). In contrast there is sufficient indication that the formation of the stacking-fault tetrahedra has a stable size below a certain temperature. The exact mechanism leading to the formation of stable nucleus is not clear. In any case, our theory provides a useful information about the nucleation time. We have defined the nucleation time τ', as the time required for the concentration of single vacancy units to reduce to a few per cent of its initial value. This definition has a simple interpretation that there are few vacancy units in each cluster on an average. This definition yields a value of 10^{-2} sec for τ' at 283°K for aluminium which agrees with the value obtained by Kiritani (1973) on computer. In his approach he defines two quantities namely the transient time and the nucleation time. Our definition of the nucleation time is the same as his transient time. The value of the nucleation time (in his definition) is larger by an order of magnitude than the transient time. We do not have an equivalent of Kiritani's nucleation time due to the nature of the decoupling used. Although we have only indirectly obtained information about the nucleation time, it does give an idea of the time scales involved. Experimentally the time scales involved can only be estimated indirectly and therefore no quantitative comparison can be made. (Kiritani *et al* 1969). A plot of the nucleation time for the formation of vacancy loops in quenched aluminium and the formation of stacking-fault tetrahedra in quenched gold is shown in figure 1. The nucleation time rapidly decreases with temperature. This should be expected as the mobility of the vacancy units increases. In all probability, the estimated nucleation time is only a lower bound.

The shape of the distribution is not realistic. Experimental curves are nearly Gaussian often with some asymmetry. However, as for the calculation of averages,
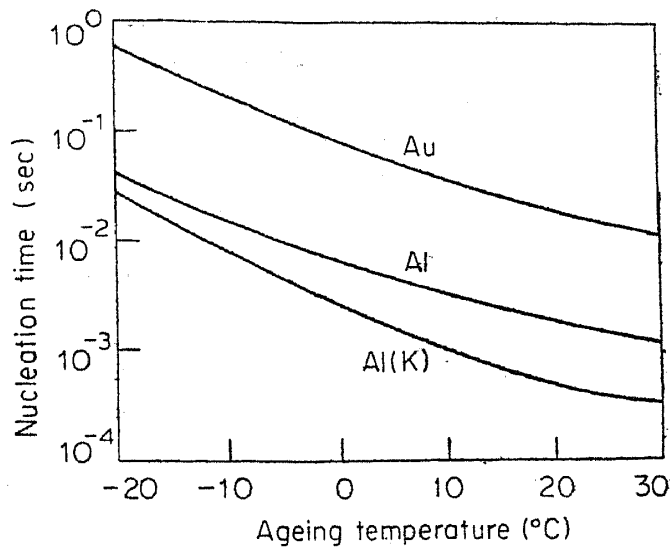
Figure 1. The nucleation time for faulted loops and stacking-fault tetrahedra in aluminium and gold respectively. The curve Al (K) corresponds to the work of Kiritani (1973).

the agreement with the experiment will be shown to be quite good. Consider the calculation of mean square number of vacancies in a cluster.

$$\langle n^2 \rangle = \sum_{2}^{\infty}{}' n^2 \frac{b^{|n-n_0|}}{|n-n_0|} \bigg/ \sum_{2}^{\infty}{}' \frac{b^{|n-n_0|}}{|n-n_0|}.$$

The prime on the summation indicates $n \neq n_0$ in the summation. The value of n_0 is generally large, at least at temperatures of interest in this paper. If we use this fact, we have

$$\langle n^2 \rangle = \sum_{-n_0+2}^{\infty}{}' (m+n_0)^2 \frac{b^{|m|}}{|m|} \bigg/ \sum_{-n_0+2}^{\infty}{}' \frac{b^{|m|}}{|m|},$$

$$\simeq 2 \sum_{1}^{\infty}{}' (m^2 + n_0^2) \frac{b^m}{m} \bigg/ 2 \sum_{1}^{\infty}{}' \frac{b^m}{m}.$$

So
$$\langle n^2 \rangle - n_0^2 = \frac{N_0(N_0 + x_2)}{x_2^2 \ln[(N_0 + x_2)/x_2]}. \tag{14}$$

Thus we see that x_2 is directly related to $\langle n^2 \rangle$ and n_0, and therefore x_2 can be regarded as a parameter to be determined from experiments. Given the value of $\langle n^2 \rangle$ and n_0 at any temperature x_2 can be determined. The total concentration of the clusters, .

$$N_S^T = \sum_{2} N_n = 4 x_2 \frac{(2N_0 + x_2)}{(N_0 + x_2)} \ln\left(\frac{N_0 + x_2}{x_2}\right). \tag{15}$$

It is clear from (14) and (15) that the temperature dependence of the total density N_S^* and the mean squared average of the number of vacancies is opposite. (If $\langle n^2 \rangle^{1/2}$ increases with temperature, n_0 also increases. However, the temperature dependence of these two quantities would be in general different.) Thus if $\langle n^2 \rangle$ increases with temperature, N_S^T decreases and vice versa.

Now if we wish to compare with experiments, a little care would be needed in identifying the theoretical distribution in n-space with the experimental distribution in the r-space. We have shown in appendix B that the total densities in n- and r-space are the same. With this identification, we shall proceed to compare the theoretical and the experimental densities. (The total density in theory is denoted by $N_S^* = Z N_S^T$, where Z is the total number of atoms per cm^{-3}.) The problem in using (14) is that $\langle n^2 \rangle$ is not generally supplied by experiments. In cases where the distribution is given, these can be easily calculated. The case of gold (Jain and Siegel 1972a) and aluminium (Kiritani 1973, Jain and Siegel 1972b) where the distributions are given will be first considered. The concentration of vacancies contained in the clusters is calculated from the experimental data using the expression $N_0 = \alpha a \langle r^2 \rangle N_S^E/4$ where N_S^E is the total density of the clusters experimentally measured, $\langle r^2 \rangle$ is the mean squared radius of the clusters and α is equal to unity for tetrahedra, and $4\pi/\sqrt{3}$ for vacancy loops. (We wish to remark that the value of N_0 that we will use for computing N_S^T will be different from that used for calculating the nucleation time for vacancy loops earlier. While computing the nucleation time, we used a value of 2×10^{-4} to facilitate comparison with the value obtained by Kiritani (1973). In the present case, the value of N_0 has to be consistent with the total number of vacancies in the clusters.) The value of $\langle n^2 \rangle^{1/2}$, n_0 and N_0 have been listed in table 3. (Table 3 also contains data as given in Kiritani 1973, Jain and Siegel 1972a, Yoshida *et al* 1963. Incidentally, there is an error in scale of the y-axis of figure 16 of Kiritani 1973. The y-axis should be multiplied by a factor 10^{11} for experimental curve and a factor of 10^{10} for the theoretical one (Kiritani 1977).) The calculated values of the total density along with the corresponding experimental values have also been listed in table 3. The agreement in the case of gold is seen to be quite good. In the case of aluminium, the theoretical values are nearly 25 times larger than the corresponding experimental values. This is due to the fact that the theoretical distribution is highly peaked in contrast to the experimental ones. In addition the experimental distributions are nearly symmetric which generally lead to small values of variance. (The value of $\langle n \rangle$ is close to n_0 in these cases. For example, in the case of aluminium quoted in column one, row three, $\langle r \rangle = 276$Å with $r_0 = 275$Å.) Thus these values

Table 3. Total density of clusters

$\langle r^2 \rangle^{1/2}$ (Å)	$\langle n^2 \rangle^{1/2}$	n_0	N_0	x_2	Total density per cm^3	
					Experimental	Theory ZN_S^T
Au[a] 410	85259	62977	3×10^{-4}	$1\cdot51 \times 10^{-9}$	$2\cdot00 \times 10^{15}$	$4\cdot34 \times 10^{15}$
Al[b] 642	193347	172897	6×10^{-5}	$1\cdot96 \times 10^{-10}$	$2\cdot00 \times 10^{13}$	$5\cdot96 \times 10^{14}$
Al[c] 276	36204	33716	$5\cdot4 \times 10^{-5}$	$1\cdot25 \times 10^{-10}$	$1\cdot00 \times 10^{14}$	$3\cdot26 \times 10^{15}$

a Jain and Siegel 1972a; b Yoshida *et al* 1963; c Kiritani 1973.

of $\langle n^2 \rangle^{1/2}$ and n_0 lead to larger theoretical densities. In the case of gold, due to the asymmetry the difference between $\langle n^2 \rangle$ and n_0 is larger than the corresponding symmetric case, i.e, a distribution with the same value of $\langle n^2 \rangle$ and n_0. Therefore the agreement is better.

Now we can consider the temperature dependence of N_S^T. In order to obtain this, we need the temperature dependence of $\langle n^2 \rangle$ and n_0. (This is necessary since x_2 is now a parameter.) Generally $\langle n^2 \rangle$ and n_0 are not given. These can be obtained in the cases where the distribution is given. The two distributions given for vacancy loops (Kiritani 1973, Yoshida *et al* 1963) indicate that there is very little asymmetry in these distributions. We take this feature and other features of these two cases to be representative at other temperatures as well. For these two cases, we find that the values of $\langle n^2 \rangle^{1/4}/\langle r^2/a^2 \rangle^{1/2}$ and $n_0^{1/2}/\langle r^2/a^2 \rangle^{1/2}$ to be very close. The values of these quantities that we have used for calculating n_0 and $\langle n^2 \rangle$ at other temperatures are 1·047 and 0·996 respectively. The data used (first four column of table 4) have been obtained from figure 18 of Kiritani (1973). We note that the concentration of vacancy units in these cases (calculated from the data using the formula $N_0 = a\alpha$ $\langle r^2 \rangle N_S^E/4$) is not constant. The values of the theoretical densities ZN_S^T at various temperatures along with the corresponding experimental values have been tabulated in table 4. A plot of the temperature dependence of the total densities is shown in figure 2. It can be seen that the theoretical and experimental curves are nearly parallel.

The time evolution of the distribution has two contributions, one of which vanishes identically as $t \to \infty$. The time required for the formation of large clusters is given by $\tau'' \sim (N_0 + x_2)/x_1 x_2^2$. The value of τ'' that we obtain for gold and aluminium are larger than the corresponding experimental values by two orders of magnitude. This is due to the fact that τ'' is sensitive to the value of x_2. The additional reason may be in the very nature of the distribution.

4. Summary and discussion

To summarise the rate equations for clustering of vacancies were written down assuming only single vacancy units to be mobile. By defining a generating function, the coupled differential-difference equations were converted into a first order partial differential equation for the generating function. Using the fact that the total

Table 4. Temperature dependence of the total density

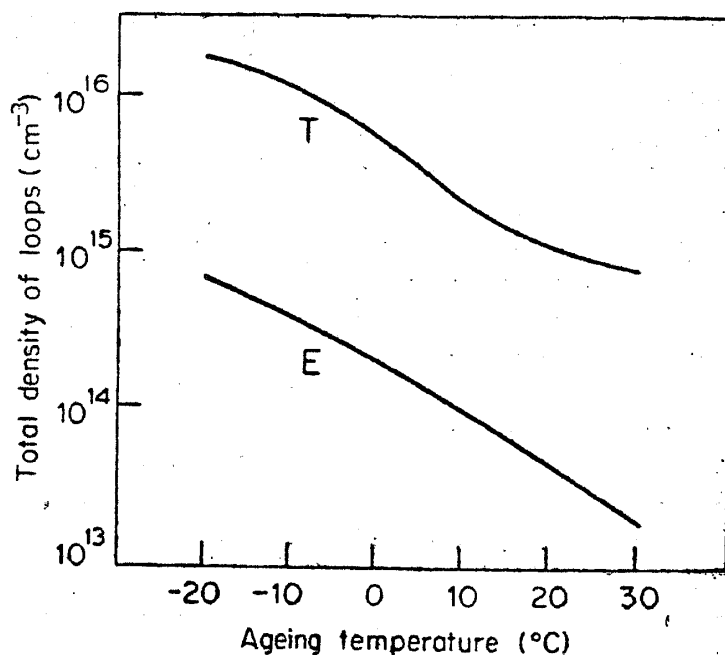| Ageing tempe- ratures (°C)	$\langle r^2 \rangle^{1/2}$ (Å)	$\langle n^2 \rangle^{1/2}$	n_0	$N_0/10^{-5}$	x_2	Total density/cm³	
						Experimental	Theory
−20	66	2173	1973	2·75	$1·1 \times 10^{-8}$	$8·6 \times 10^{14}$	$2·1 \times 10^{16}$
−10	97	4591	4131	4·11	$6·89 \times 10^{-9}$	$6·2 \times 10^{14}$	$1·46 \times 10^{16}$
0	150	10976	9887	4·36	$3·40 \times 10^{-9}$	$3·0 \times 10^{14}$	$7·9 \times 10^{15}$
10	276	36204	33716	5·4	$1·25 \times 10^{-10}$	$1·0 \times 10^{14}$	$3·2 \times 10^{15}$
20	438	93082	84296	9·4	$6·2 \times 10^{-10}$	$6·8 \times 10^{13}$	$1·6 \times 10^{15}$
30	790	302812	274238	13·4	$2·95 \times 10^{-10}$	$3·2 \times 10^{13}$	$9·2 \times 10^{14}$

P.—9

Figure 2. Temperature dependence of the total density of clusters.

number of the vacancies is conserved, an exact solution for the decay of the concentration of single vacancy units was obtained. The form of the solution is exponential with a short time constant. This allows us to decouple it from the differential equation for the generating function. The solution of N_1 apart from giving the nucleation time for small clusters, also suggests that the collapse time for cascades produced during irradiation would be $(N_c x_1)^{-1}$ where N_c is the local concentration of the vacancies produced during irradiation. This time is expected to be of the order of 10^{-2} to 10^{-4} sec at $300°C$ in aluminium if we assume $N_c \sim 10^{-4}$ to 10^{-6}. Then, the solution of the differential equation for the generating function was obtained. The distribution function which was obtained by inverting the generating function predicts the total density as a function of temperature and time given $\langle n^2 \rangle$ and n_0 as a function of temperature. The results agree well with the experiments. The theory also predicts the characteristic time required for the formation of large clusters.

We shall recall the idealisations and approximations made in obtaining the solution of the problem and comment on them. The number of absorption (and emission) sites has been taken to be proportional to $n-1$ (and n) in order to facilitate decoupling as has been mentioned earlier. In the case of vacancy loops the number of absorption sites and emission sites are functions of the size of the loop and for small size it is linear in n, changing over to $n^{1/2}$ for large sizes. From the connection that we have investigated between the solution of differential-difference equation and the associated continuum equation, it appears that this may be one of the factors contributing to the non-evolution of the peak. The major idealisation in modelling the physical situation is in the assumption about the binding energy of a vacancy unit being independent of the size of the cluster. Some justification has been offered in §1. The idealisation is possibly another factor responsible for the unphysical features of this distribution. In a separate paper (paper No. III) we shall see how the unphysical nature of the distribution can be overcome. The quantity x_2 is dependent on $\langle n \rangle$

and has to be regarded as a parameter, and therfore many factors which have not been taken into consideration while modelling such as the effect of impurities, the presence of various kinds of sinks has been taken care of (at least partially), since these have a direct effect on the sizes of the clusters and the total densities which are in turn a function of x_2.

Two approximations have been made in obtaining the solution of the differential equation for the generating function. The first one is to ignore the term containing N_2. The justification for this has been given in appendix A. The other approximation is the decoupling approximation, wherein we use only the asymptotic value N_1 to solve for $X(Z, t)$. This approximation assumes that there is a smooth evolution of $N_n(t)$ for shorter times which matches with the solution obtained at the start of the growth process (i.e., after N_1 has reached its asymptotic value). This statement appears to be justified since the solution $N_n(t)$ obtained is consistent with the initial condition that we have used in obtaining the solution $X(z, t)$. This is to be expected for two reasons namely, first, the decay time for N_1 to reach its asymptotic value is very small and second, after decoupling, the vacancy units redistribute themselves among the several clusters. Thus the evolution clusters proceeds in a smooth way. This is supported by experiments done by Jain and Siegel (1972a). For shorter times the theory is incapable of predicting the distribution. However, there may be short transients superimposed on the present solution obtained. This aspect can be seen from the fact that $N_n(t)$ goes to zero as t is allowed to go to zero.

Acknowledgements

Appendix A

In this appendix we shall outline the method of obtaining the solution of the differential equation for the generating function. At the outset we wish to state that we have been able to obtain the solution only if the term containing N_2 can be disregarded and over the interval of time after N_1 has reached its asymptotic value. Consider the equation without N_2 term. Later we shall provide some justification for this assumption that ignoring the term containing N_2 does not affect the solution of $X(Z, t)$ seriously. First, we observe that even with this assumption, this equation cannot be solved in closed form if the full time dependence of N_1 is used. Fortunately N_1 has a very short time constant and N_1 attains its asymptotic value in less than a second. So we could use the asymptotic value of N_1 in (8) and solve the differential equation assuming that there is some kind of a smooth evolution of the clusters for time interval shorter than this. This would mean that we have to extend the time domine upto zero. Using the asymptotic value of N_1 in (8) we get

$$\frac{\partial X}{\partial t} = aZ^{-2} + c(Z-1)(b-Z)\frac{\partial X}{\partial Z}, \qquad \text{(A.1)}$$

where the constants are

$$b = N_0/(N_0 + x_2), \quad c = x_1 x_2 \text{ and } a = x_2 c b^2/2.$$

The subsidiary system of equations take the form

$$\frac{dt}{1} = \frac{dZ}{c(Z-1)(Z-b)} = \frac{d\chi}{dZ^{-2}}$$

The solution for these equations are

$$\chi - \frac{a}{c}\left[-\frac{1}{bZ} + \frac{1+b}{b^2} \ln \frac{Z}{Z-b} + \frac{1}{1-b} \ln \frac{Z-1}{Z-b} \right] = K', \tag{A.2}$$

and

$$\frac{Z-1}{Z-b} \exp\left[-c(1-b)t\right] = \frac{Z-1}{Z-b}\phi\,(t) = K''. \tag{A.3}$$

Eliminating k' and k'' from the above two equations we get

$$\chi(Z, t) = \frac{a}{b}\left[\frac{1+b}{b^2} \ln \frac{Z}{Z-b} + \frac{1}{1-b} \ln \frac{Z-1}{Z-b} - \frac{1}{bZ} \right] + F\left(\frac{Z-1}{Z-b}\phi\,(t)\right), \tag{A.4}$$

where $F(y)$ is an arbitrary function of its argument to be determined by using the initial conditions. At $t=0$, all N_n are zero except $n=1$, which implies that $\chi(Z, t)=0$. At this point it may be appropriate to point out the apparent inconsistency of using the asymptotic value of N_1 and using the initial condition $\chi(Z, t)=0$. After having used asymptotic value of N_1, we do not expect the solution of $\chi(Z, t)$ to be valid for times shorter than the time required for N_1 to reach its asymptotic value. (Note that this is less than a second.) Therefore there will be inconsistency for shorter times, in particular at $t=0$. ($t=0$ is a point in this region.) If the full time dependence of N_1 was used, then it is clear that more and more single vacancy units would flow back from N_n to N_1. Thus by disregarding the time dependence of N_1, we have prevented the back flow and therefore cannot account for some vacancy units in this region, in particular $N_0 - N_1 (\infty)$ vacancy units at $t=0$. (An alternate initial condition that suggests itself as a possibility is to use $\chi(Z, 0) = N_0^2/(N_0 + x_2)$ which means that at $t=0$ itself so many clusters are formed. Apart from the fact that this would be unphysical, it also raises a question about the distribution for N_n to be used for computing $\chi(Z, 0)$ which is required for the initial condition. Thus we will use $\chi(Z, 0)=0$ as the initial condition. As we see later, this condition gives N_n which is consistent with the initial condition i.e., as $t \to 0$, $N_n \to 0$.) With these remarks in mind, we shall use the condition $\chi(z, 0)=0$. Then the solution that we obtain is

$$\chi(Z, t) = \frac{a}{c}\left\{ \frac{1+b}{b^2} \ln\left[\frac{Z(1-b)}{Z-b-\phi b(Z-1)} \right] + \frac{1}{1-b} \ln \phi - \frac{1}{bZ} \right.$$

$$\left. + \frac{\phi(Z-1)+b-Z}{b[b-Z+\phi b(Z-1)]} \right\}. \tag{A.5}$$

Now we shall consider the justification that can be offered in support of the assumption that throwing away the term containing N_2 should not affect the solution of $\chi(Z, t)$ seriously. First, recall that we solve for $\chi(Z, t)$ only after N_1 reaches its asymptotic value. By this time several clusters would have formed and N_2 happens to be just one of them. Thus ignoring the term $x_1 x_2 N_2 (Z^{-2} - 2 Z^{-1})$ may change only the magnitude of the coefficient N_n in the expansion of $\chi(Z, t)$, since this term is equivalent to a source term. However, the total number of vacancy units contained is proportional to $2N_2$, whereas, $\chi(Z, t)$ contains several N_n. Thus ignoring this term should have very little effect on $\chi(Z, t)$. Further there are other terms which contain N_2 in the equation for $\chi(Z, t)$. These terms arise from

$$- \frac{\partial \chi}{\partial Z} x_1 x_2 (Z-1)(Z-b),$$

and give a contribution of

$$+2Z^{-3} x_1 x_2 N_2 (Z-1)(Z-b).$$

The term with the coefficient Z^{-1} cancels the corresponding term in the source term. The other terms are, however, larger by a factor of two. Thus the number of vacancy units that we have ignored (contained in the term N_2) is small. In addition the value of N_2 at the beginning of the process of growth of the clusters is small. This can be seen by the following argument. We shall first argue that N_2 would have reached equilibrium with N_1 by the time N_1 reaches its asymptotic value. Since N_1 is monotonically decreasing and since we have used the asymptotic value of N_1 (due to its short time constant), it means that N_1 has attained equilibrium with the remaining clusters, particularly with N_2. Only a redistribution among the various clusters can occur and any vacancy emitted from N_2 or any other clusters is to be interpreted as going into another cluster. This is due to the fact N_1 has already reached its asymptotic value. (It may be noted that a similar argument would not hold for shorter times.) Thus N_1 is in equilibrium with N_2 and therefore, it is most likely to be of the order $N_1^2 \exp b_2/kT$, where b_2 is the binding energy of the divacancy unit. Thus the number of vacancy units contained in this term is small right at the beginning of the process of clustering. (Note that there is possibly a time dependence of N_2. This may give raise to a short transient.) Also we wish to stress that there may be some effect of this approximation on the value of N_2 at any instant of time, but we would not be interested in small clusters, since $\langle n \rangle$ is of the order of 10^5.

Appendix B

In this appendix we will show that the total density of the clusters measured in n-space is equal to the total density of clusters in r-space. This follows from the fact that the total number of vacancy units in both the spaces should be the same. Consider the concentration of vacancies in the clusters in n-space.

$$f(t) = c_v = \sum n N = \int n N(n) \, dn,$$

where $N(n)$ is the concentration of clusters in this space.   Using the relation $n = ar^2/a^2$ ($a = 1$ for tetrahedra and $a = 4\pi/\sqrt{3}$ for loops), we have

$$C_v = a^2 \int \frac{r^2}{a^2} N\ (ar^2/a^2) \frac{2rdr}{a^2}. \tag{B.1}$$

The experimental distributions are measured in r- or in L-space and the concentration of vacancies stored in the clusters is given by

$$C_v = a \left< r^2 \right> \overline{N}_s\ a/4, \tag{B.2}$$

where $\overline{N}_s$ is the number density or the total density per cm^{-3} in r-space.

$$C_v = a\ a/4 \int r^2\ \overline{N}^d\ (r)dr = aa \int r^2/a^2\ \overline{N}^c\ (r)dr/a. \tag{B.3}$$

The distribution of clusters

$$\overline{N}^d\ (r) = 4/a^3\ \overline{N}^c\ (r)$$

is in r- space (per cm^{-3} per Angstrom unit), and $\overline{N}^c(r)$ is the corresponding concentration.   Comparing (B.1) and (B.3), we have

$$2\ a\ r/a^2 N(r^2/a^2) = \overline{N}^c\ (r).$$

The total density of vacancy clusters in n-space is

$$Z \int N(n)dn = \int N^*(n)dn = 2a \int rdr/a^2\ zN(r^2/a^2)$$

$$= \int 2a\ rdr/a^2\ N^*\ (r^2/a^2) = \int \overline{N}^d\ (r)\ dr = \overline{N}^d. \tag{B.4}$$

Thus the total density in n and r-spaces are equal.

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