

Monod defect Annealing Kinetics*

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The range of validity of the diffusion equation in describing point-defect annealing kinetics is examined, and it is concluded that even for sinks of atomic dimensions, the solutions of the diffusion equation which correspond to zero thermal excess concentration at sink sites give a good account of the annealing behavior. The annealing of point defects to stacking-fault tetrahedra, dislocation loops, and to dislocations which are allowed to climb, is then treated by means of equations which describe the annealing in the presence of time-dependent sink properties, using also an electrostatic approximation to sink efficiencies. Finally, the problem of void stability is discussed.

I. INTRODUCTION

IF point defects are introduced into a crystalline solid, then at temperatures at which the defects are mobile, they migrate through the lattice and are gradually annihilated at faults in the crystalline structure. These "sinks" may be extended in space as in the cases of crystal boundaries or dislocations, or more localized in the form of voids, stacking-fault polyhedra, or dislocation loops. The sinks absorb the point defects with efficiencies which depend on the individual sink characteristics and which, as originally pointed out by Seitz,¹ may be modified by the absorption process. Given an initial excess defect population $c(\mathbf{r})$ above the thermal equilibrium value c_0 , the various types of sink present in a particular region complete in a complicated fashion in reducing the excess population to zero. Since the point-defect population may be monitored as a function of annealing time, and also, the sink characteristics may in many cases be observed, theoretical predictions concerning the point-defect loss as a function of annealing time become of considerable interest.

Our approach to the kinetics of defects in a lattice is made through the diffusion equation. We first examine the applicability of this macroscopic equation in the presence of static sinks whose dimensions may be only of the order of magnitude of the lattice spacing. A more general description of the annealing is then developed to include sinks whose dimensions are time-dependent. Finally, we give quantitative discussions of the annealing characteristics in the presence of the various types of sink known to take part in reducing the point-defect population of metals to its thermal equilibrium value.

II. THE DIFFUSION PROCESS

It is assumed that the point defects are distributed among a set of lattice points individually identified by means of a subscript. At any time t , the occupation number $\sigma_n(t)$ of the n th site is either 1 or 0. By averaging over an ensemble of equivalent systems, the occupation number $\sigma_n(t)$ may be reduced to a probability $p(\mathbf{r}_n, t)$ of occupation at time t of the site n at position \mathbf{r}_n . The

probability of a defect jumping from the site n to the nearest neighboring site l is then $p(\mathbf{r}_n, t)[1 - p(\mathbf{r}_l, t)]\tau_{nl}^{-1}$ with τ_{nl} the jump time from n to l . If the jump time $\tau_{nl} = \tau$ for all neighboring n and l , the flux of defects leaving the n th site is described by the partial difference equation

$$\sum_l \{p(\mathbf{r}_n, t) - p(\mathbf{r}_l, t)\} \tau^{-1} = -\partial p(\mathbf{r}_n, t) / \partial t, \quad (1)$$

with the sum extending over all neighbors l of n . It should be noted that the assumption of equal jump times for all jump paths not only restricts us to a treatment of diffusion in the good crystal, but also excludes from the discussion any effects of interactions between the point defects (and hence of chemical gradients) or between point defects and strain fields.

Equation (1) may be separated with eigenvalues α_m to give solutions

$$p_m(\mathbf{r}_n, t) = p_m(\mathbf{r}_n) \exp(-\alpha_m^2 D t), \quad (2)$$

with $p_m(\mathbf{r}_n)$ the solution of

$$\sum_l \{p_m(\mathbf{r}_n) - p_m(\mathbf{r}_l)\} \tau^{-1} = \alpha_m^2 D p_l(\mathbf{r}_n). \quad (3)$$

For given boundary conditions the solutions $p_m(\mathbf{r}_n)$ corresponding to different eigenvalues are evidently orthogonal, since Eq. (3) may be written

$$\sum_l a_{nl} p_m(\mathbf{r}_l) = \alpha_m^2 D p_m(\mathbf{r}_n), \quad (4)$$

where a_{nl} is symmetric and has orthogonal eigenvectors. Thus,

$$\sum_n p_l(\mathbf{r}_n) p_m(\mathbf{r}_n) = A_{lm} \delta_{lm}; \quad \alpha_l^2 \neq \alpha_m^2. \quad (5)$$

In what follows we assume that the $p_l(\mathbf{r}_n)$ are orthogonal, with $A_{lm} = 1$.

In the case of a simple cubic lattice

$$\sum_l \{p_m(\mathbf{r}_n) - p_m(\mathbf{r}_l)\} = -\delta^2 p_m(\mathbf{r}_n) \quad (6)$$

with

$$\delta^2 = \delta_x^2 + \delta_y^2 + \delta_z^2$$

and the δ_x^2 are second divided-difference operators

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¹ F. Seitz, Phys. Rev. **79**, 890 (1950).

parallel to the cubic axes. If a is the lattice spacing,

$$\delta_x^2 = a^2 \frac{d^2}{dx^2} - (a^4/12) \frac{d^4}{dx^4} + \dots \quad (7)$$

Equation (1) therefore leads to the equation

$$D\nabla^2 p_m(\mathbf{r}_n) + O(a^4) = \partial p_m(\mathbf{r}_n)/\partial t, \quad (8)$$

with $D = a^2/\tau$, which reproduces the diffusion equation in the approximation that terms $\sim a^4(d^4/dx^4)$ are negligible. To the same approximation, the functions $p_m(\mathbf{r}_n)$ become the familiar continuous solutions of the wave equation which are the functions used in the usual eigenfunction expansion approach to the solution of the diffusion equation for a continuum.²

If the approximate solution $p(r) = p_0(1 - b/r)$, appropriate to the case of a spherical sink of radius b , is substituted into Eq. (8), the fourth-order operator produces a g function of amplitude $\sim a^4/r^4$ with an angular dependence given by the first Kubie harmonic together with a small spherical symmetrical part. In this way the higher-order terms introduce the lattice symmetry into the diffusion in a fashion which is significant only in the case of small sinks when $r \sim a$. Since the $p_m(\mathbf{r}_n)$ are eigenfunctions of the scalar Helmholtz equation and therefore oscillatory functions of $\alpha_m r$, the diffusion equation also breaks down for large eigenvalues such that $\alpha_m a$ is comparable with unity.

In order to obtain a more general result, we Taylor expand $p_m(\mathbf{r}_n)$ round \mathbf{r}_n to give

$$p_m(\mathbf{r}_n) - p_m(\mathbf{r}_l) = -\mathbf{l} \cdot \nabla p_m(\mathbf{r}_n) - \frac{1}{2} \nabla \cdot \mathbf{L} \cdot \nabla p_m(\mathbf{r}_n) - \dots \quad (9)$$

with $\mathbf{L} = \mathbf{l}\mathbf{l}$ and \mathbf{l} the vector between the sites n and l . The term

$$\sum_l \mathbf{l} \cdot \nabla p_m(\mathbf{r}_n)$$

vanishes from reflection symmetry, leading in an approximation analogous to that involved in Eq. (8), to the general diffusion equation

$$\nabla \cdot \mathbf{D} \cdot \nabla p_m(\mathbf{r}_n) = \partial p_m(\mathbf{r}_n)/\partial t \quad (10)$$

with

$$\tau \mathbf{D} = \sum_l \mathbf{l}\mathbf{l},$$

the sum extending over all nearest neighbors. For defects diffusing on bcc or fcc lattice sites, \mathbf{D} reduces once more to the scalar a^2/τ .

The analysis given above shows that the annealing of point defects out of a perfect crystal may always be described by the exponential decay of components whose space variations are proportional to the eigenfunctions of the difference equation, Eq. (3). For

eigenvalues α_m such that $\alpha_m^2 a^2 \ll 1$ the difference equation (1) reduces to the diffusion equation (10) except in the neighborhood of small sinks. Since the solutions of the diffusion equation are oscillatory functions of $\alpha_m r$, this criterion states that the diffusion equation approximation to Eq. (1) is valid except near small sinks, for eigenfunctions having a period occupying several lattice distances or more. We do not have cause to use the higher eigenfunctions of Eq. (1), since they correspond to extremely abrupt changes in point defect density, and therefore to unobservably short annealing times.

III. THE BOUNDARY CONDITIONS AT SINKS

To the extent that the sinks maintain the thermal equilibrium concentration of defects in the lattice, they may be thought of as regions occupied by this thermal equilibrium concentration, so that the excess population $p_m(\mathbf{r}_n)$ is zero at sites in the sinks. However, the diffusion equation breaks down for jump paths involving sink sites because the jump times are not equal in the different directions. The boundary conditions which determine the eigenfunctions must therefore be applied at the sites neighboring the sinks, and are evidently of the general amplitude to derivative type, the amplitude specifying the jump rate of defects into the sink and the derivative corresponding to the defect flow rate to sites neighboring the sink by diffusion in the good crystal.

The distinction between the condition $p_m(\mathbf{r}_n) = 0$ at sink sites and the correction boundary condition is negligible except for sinks whose dimensions are of the order of magnitude of the lattice spacing. To illustrate this fact together with the breakdown of the diffusion equation near small sinks we have computed the smallest eigenvalue of Eq. (3) (which describes the annealing of virtually all the defects in an initially uniform distribution) for sinks which comprise an atom and the first few of its neighboring shells in a spherical fcc crystal of radius R at whose periphery the boundary condition $[dp_1(\mathbf{r})/dr]_R = 0$ has been used. The computation was effected by obtaining from Eq. (1) simultaneous equations appropriate to the steady state, interrelating the occupation probabilities at various shells near the sink, and fitting these local probabilities smoothly onto a solution of the diffusion equation giving the same flow rate. For sinks composed, respectively, of an atom and its neighbors and an atom and its first three neighboring shells, the true flow rate proved to be 58% and 95% of that found on using the diffusion equation together with the boundary condition $p_m(\mathbf{r}) = 0$ at sink sites. Thus, even for very small sinks, the diffusion equation gives a sensible estimate of the defect flux, and for sinks having dimensions of several lattice distances, the error is negligible.

The geometry involved in the interesting case where dislocations act as sinks is too complex to permit as

² See, for example, J. Crank, *The Mathematics of Diffusion* (Oxford University Press, New York, 1956).

precise a discussion as that given above for spherical symmetry. However, one may note that the number of jump paths to the edge of a dislocation in an fcc crystal is about ten per site on the edge, so that the local kinetics constitute only a small restraint on the rate at which random walking to a dislocation may occur, and the loss rate may therefore be only a little slower than that predicted using the diffusion equation and a reasonable dislocation "radius" as in the treatment by Koehler, Seitz, and Bauerle.³ This is to be contrasted with the results of a method of estimation due to Damask and Dienes⁴ who assume that at all times, the point defects and sinks are randomly dispersed throughout the good crystal so that the loss rate is proportional to the average excess probability of occupation of a defect site multiplied by the number of jump paths terminating in the sink. The neglect of gradients driving the annealing and consequent overestimation of the probability of defects being close to the dislocation causes this latter method to predict a defect loss rate a factor of 10^2 faster than the value found using the lowest eigenvalue of the diffusion equation with typical values of dislocation density $\sim 10^8$. A similar type of error, made in the calculation of the value of an assumed eigenvalue, invalidates the conclusions of Kimura, Maddin, and Kuhlmann-Wilsdorf.⁵

IV. TIME-DEPENDENT BOUNDARY CONDITIONS

The standard method of solving diffusion problems is to make an expansion of the defect distribution at time $t=0$ in terms of eigenfunctions which satisfy the boundary conditions.² Provided that the boundary conditions do not change, the exponential decay of these eigenfunctions then describes the subsequent behavior of the system. In this way solutions have been obtained for the annealing of defects out of the surface of samples having various symmetries. The main characteristic of these systems is the behavior at short times when the average occupation probability over the sample may be shown to obey the equation

$$\bar{p}(t) = p_0(1 - 2(Dt/\pi)^{1/2}A/V), \quad (11)$$

where p_0 is the initial probability (assumed uniform), A is the surface area, and V the sample volume. This equation describes up to half the annealing in regions having smooth surfaces, the last fraction of the annealing tending towards the simple exponential decay associated with the smallest eigenvalue alone.⁶

³ J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

⁴ G. J. Dienes and A. C. Damask, Discussions Faraday Soc. **31**, 29 (1962).

⁵ H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, Acta Met. **7**, 145 (1959).

⁶ The possibility of using this latter property to measure the diffusion coefficient of defects has been noted by A. Blandin and J. Friedel, Acta Met. **8**, 384 (1960).

When the annealing is caused by many localized sinks, it is observed that a maximum in the occupation probability occurs between the sinks.^{7,8} A region of the lattice is then assigned to each sink and an eigenfunction expansion made in each region, satisfying the boundary conditions near the sink and having zero gradient at the surface of the region. In this way an approximate solution of the annealing is obtained. However, if the sink properties are time-dependent, the method breaks down because the eigenfunctions do not satisfy the boundary conditions at all times. In what follows, we develop a procedure by means of which the annealing may be determined under these circumstances.

Let us take an orthonormal set of functions

$$p_m(\mathbf{r}_n, t, t') = p_m(\mathbf{r}_n, t) \exp[-\alpha_m^2(t)D(t)(t'-t)] \quad (12)$$

of which the $p_m(\mathbf{r}_n, t)$ are eigenfunctions of Eq. (3) having eigenvalues $\alpha_m(t)$, and which satisfy the boundary conditions at $t'=t$. For a given distribution of defects at $t'=t$, namely,

$$p(\mathbf{r}_n, t) = \sum_l \beta_l(t) p_m(\mathbf{r}_n, t) \quad (13)$$

the distribution change at time $t'=t+\delta t$ is

$$\delta p(\mathbf{r}_n, t+\delta t) = -\sum_m [\beta_m(t) - \beta_m^0(t)] \times p_m(\mathbf{r}_n, t) \alpha_m^2(t) D(t) \delta t, \quad (14)$$

where we have taken the thermal equilibrium defect distribution at t to be

$$p_0(\mathbf{r}_n, t) = \sum_m \beta_m^0(t) p_m(\mathbf{r}_n, t) \quad (15)$$

and have assumed that δt is sufficiently small that the exponential could be expanded as shown.

The distribution at $t+\delta t$ may also be expressed in terms of eigenfunctions $p_m(\mathbf{r}_n, t+\delta t)$ which satisfy the boundary conditions at $t+\delta t$:

$$\begin{aligned} p(\mathbf{r}_n, t+\delta t) &= \sum_m \beta_m(t+\delta t) p_m(\mathbf{r}_n, t+\delta t) \\ &\cong \sum_m \left[\beta_m(t) \frac{\partial p_m(\mathbf{r}_n, t)}{\partial t} + \frac{\partial \beta_m(t)}{\partial t} p_m(\mathbf{r}_n, t) \right] \delta t. \end{aligned} \quad (16)$$

On equating Eqs. (16) and (14), multiplying each side by $p_m(\mathbf{r}_n, t)$, and summing over all n we find

$$\begin{aligned} \frac{d\beta_m(t)}{dt} &= -\alpha_m^2(t) D(t) [\beta_m(t) - \beta_m^0(t)] \\ &\quad - \sum_l \beta_l(t) \sum_n \frac{\partial p_l(\mathbf{r}_n, t)}{\partial t} p_m(\mathbf{r}_n, t). \end{aligned} \quad (17)$$

⁷ F. S. Ham, Phys. Chem. Solids **6**, 335 (1958).

⁸ G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957), p. 143.

The last term on the right of Eq. (17) may be rewritten in terms of a parameter $\zeta(t)$ which measures the changing sink properties—say the dislocation climb or the edge of a stacking fault tetrahedron, to yield

$$\frac{d\beta_m(t)}{dt} = -\alpha_m^2(t)D(t)[\beta_m(t) - \beta_{m0}(t)] - \frac{d\zeta}{dt} \sum_i \beta_i(t) \sum_n \frac{\partial p_i(\mathbf{r}_n, t)}{\partial \zeta} p_m(\mathbf{r}_n, t). \quad (18)$$

In the event of a continuous production of defects occurring as in radiation damage experiments, an additional term $\partial\beta(t)/\partial t$ must be included on the right side of Eq. (18). We note that by definition

$$\sum_n p_m(\mathbf{r}_n, t) p_i(\mathbf{r}_n, t) = \delta_{im},$$

$$\sum_n \frac{\partial p_m(\mathbf{r}_n, t)}{\partial \zeta} p_i(\mathbf{r}_n, t) = -\sum_n p_m(\mathbf{r}_n, t) \frac{\partial p_i(\mathbf{r}_n, t)}{\partial \zeta} \quad (19)$$

and

$$\sum_n \frac{\partial p_m(\mathbf{r}_n, t)}{\partial \zeta} p_m(\mathbf{r}_n, t) = 0.$$

The set (17) of coupled differential equations may in principle be solved to yield a complete description of the annealing behavior. In practice, however, this is not possible, and it is necessary to approach the solution in approximate fashion in order to obtain information concerning various sink properties.

V. THE ELECTROSTATIC APPROXIMATION

Ham⁷ has pointed out that to the extent that a steady state is established in the diffusion of atoms to a sink region, the diffusion equation may be approximated by Laplace's equation and the loss rate found from the solutions of the latter equation. A neat statement of this observation is that the effective radius of any geometry of localized sink is equal to the electrostatic capacity of a conducting body having the same dimensions as the sink.

If we substitute the solution of Laplace's equation,

$$p(\mathbf{r}) = \sum_{n,m} s_{nm} r^{-n-1} P_n^m(\cos\theta) \begin{cases} \sin m\varphi \\ \cos m\varphi \end{cases}, \quad (20)$$

into the space part of the separated diffusion equation

$$\nabla^2 p(\mathbf{r}) = -\alpha^2 p(\mathbf{r}) \quad (21)$$

then terms on the left are $\sim r^{-n-3}$ and on the right $\sim \alpha^2 r^{-n-1}$ so that for small r , the terms on the left are much larger than that on the right, and therefore the cancellation of the left side occurring in Laplace's equation is satisfactory for small r for the diffusion equation also. In fact the spherically symmetric solution

of the diffusion equation may be expanded as

$$p_i(\mathbf{r}) = p_0(b/r + \alpha_i^2 r^2/6 - \dots), \quad (22)$$

where b is the radius of the special sink. If a radius ρ exists such that $\rho^3 \alpha_i^2 \ll 6b$ and $s_{nm} \rho^{-n} \ll s_{00}$ for all n and m , we can fit the solutions of Eqs. (22) and (20) together at ρ with $s_{00} = b$, the radius of the equivalent spherical sink which we shall call the effective sink radius. Comparing the probability distribution of Eq. (20) with the potential distribution about a charged conductor of the same dimensions as the sink, which may be obtained by replacing $p(\mathbf{r})$ by $V(\mathbf{r})$ and S_{nm} by q_{nm} , the latter being the charge multipole distribution, we note that $q_{00} = CV_0$ with C the capacity and V_0 the potential of the conductor. Hence by equating $p(\mathbf{r})/p_0$ to $V(\mathbf{r})/V_0$, we find that the effective sink radius is equal to the electrostatic capacity as stated above. Since the eigenvalue of the slowest annealing eigenfunction is closely given by $3b/R^3 = \alpha_1^2$ where R is the radius of the region being voided by the sink, the rate at which the great majority of the defects are absorbed may be determined simply by referring to the capacity of a body of the appropriate geometry. The values obtained by Ham of the eigenvalues for ellipsoids of revolution are readily reproduced in this way from the well-known capacities of these bodies.

The conditions under which the solutions of Eqs. (20) and (22) may be fitted together are not too stringent in practice, for the first condition is reasonably well satisfied in the case of the smallest eigenvalue even for ρ as large as $R/2$. The second requirement is either of high sink symmetry or that the sink be considerably smaller than R , corresponding to the need for sinks which are well separated in comparison to their dimensions. For the larger eigenvalues, the situation is more difficult, but as stated previously, the higher-order eigenfunctions are irrelevant to the annealing except for the small initial transient which they produce.

VI. STACKING FAULT POLYHEDRA

In gold quenched from temperatures above 800°C, tetrahedra whose faces are stacking faults with edges of stairrod dislocations are observed to form and act as sinks for vacancies.⁹ The precise mechanisms of nucleation and growth are not at present clear, but the former has been linked convincingly with the presence of small clusters in the lattice by de Jong and Koehler,¹⁰ while the growth has been discussed in terms of ledges moving across the faces of the polyhedron.^{10,11} Because of the nucleation conditions, growth has been observed only in the presence of mixed single and divacancy annealing, for which accurate solutions of the diffusion equations are not at present available. It seems likely that

⁹ R. M. J. Cotterill, *Phil. Mag.* **6**, 1351 (1961).

¹⁰ M. de Jong and J. S. Koehler, *Phys. Rev.* **129**, 49 (1963).

¹¹ H. Kimura, D. Kuhlmann-Wilsdorf, and R. Maddin, *Appl. Phys. Letters* **3**, 4 (1963).

the growth mechanism will be most readily elucidated from measurements involving quenching of samples already containing the tetrahedra, from sufficiently low temperatures that single vacancies dominate the annealing. In what follows we discuss some simple possibilities of this latter type of kinetics.

Let us first assume that the defects are absorbed at the surfaces, presumably by virtue of the ledges sweeping along and collecting the point defects neighboring the surface. The electrostatic capacity of a conducting tetrahedron is about $c/2$ where c is the edge of the tetrahedron. The smallest and most important eigenvalue of the diffusion equation is then

$$\alpha_1^2(t) = 3c(t)/2R^3 = 2\pi c(t)N_s, \quad (23)$$

where N_s is the number of tetrahedra per unit volume. The number of vacancies contained in a tetrahedron of edge $c(t)$ is about $c^2(t)/a^2$ with a the lattice spacing, as may be seen from the fact that an increment $\delta c = a/\sqrt{2}$ in edge length results from the addition of $\delta N = \sqrt{2}c/a$ vacancies. If $N(t)$ is the thermal excess number of free vacancies per tetrahedron and N_0 is the number contained in a tetrahedron when the annealing is completed,

$$dN/dt = \pi N_s D \alpha N (N_0 - N)^{1/2} \quad (24)$$

for which the solution having $N = N_1$ at $t = 0$ is

$$2\pi N_0^{1/2} N_s D \alpha t = \tanh^{-1}[(N_0 - N)/N_0]^{1/2} - \tanh^{-1}[(N_0 - N_1)/N_0]^{1/2}. \quad (25)$$

For small quenched-in concentrations $N_1 \ll N_0$ and c does not change significantly during the annealing, so that Eq. (25) reduces to

$$N = N_1 \exp[-2\pi c N_s D t]. \quad (26)$$

The absorption of defects may occur in the neighborhood of the corner of the tetrahedron rather than at the faces. If we specify a radius b of the region round each corner at which absorption occurs, then from the capacity

$$C \simeq 4b(1 - 3b/c) \quad (27)$$

of the equivalent conductor, we obtain the annealing equation

$$dN/dt = 16\pi N N_s b(1 - 3b/c)D. \quad (28)$$

To the extent that $b \ll c$, one then finds that the defect population is described by

$$N = N_1 \exp[-16\pi N_s b D t]. \quad (29)$$

If, on the other hand, the corner and the stairrod dislocations are the operative parts of the sink, the absorption rate is more difficult to estimate without indulging in a fairly lengthy computation of the capacitance appropriate to this geometry. It is evident, however, that the absorption rate will be intermediate between the values given by Eqs. (26) and (29), and show a dependence on c which is not exhibited in the case of annealing to the corners alone for $b \ll c$.

VII. DISLOCATION LOOPS

Both vacancies and interstitials have been observed to condense to form a plane defect bounded by a dislocation loop and in both cases the defect acts as a sink which absorbs further point defects at the expense of an increased length of dislocation. As in the case of stacking-fault tetrahedra, the exact absorption mechanism remains obscure, two limiting cases appearing to be that the point defects are annihilated only at the dislocation or that the plane defect absorbs at all points, with diffusion of trapped point defects along the plane to the dislocation occurring with sufficient speed that their temporary presence on the surface does not affect further absorption.

To determine the absorption rates in the two cases we need, respectively, the electrostatic capacity of a torus having the same radius ρ_0 as the dislocation loop, and cross-sectional radius ρ of atomic dimensions, or the capacity of a disk radius ρ_0 and of negligible thickness. The former is¹²

$$C_t = -\frac{4}{\pi}(\rho_0^2 - \rho^2)^{1/2} \sum_{m=0}^{\infty} Q_{-1/2+m}(2\rho_0/\rho)/P_{-1/2+m}(2\rho_0/\rho) \quad (30)$$

while the latter takes the form

$$C_d = 2\rho_0/\pi. \quad (31)$$

As before, the absorption rate of point defects follows as

$$dN/dt = 4\pi C_\alpha N_\alpha D N, \quad (32)$$

where C_α and N_α are the capacities and concentrations per unit volume of the particular type of sink specified by α . In the case of the disk, Eq. (32) reproduces the result found by Ham in a study of precipitation phenomena. As stressed by Ham,⁷ the effects of growth of these types of sink are well represented by simply including the time dependence of the lowest eigenvalue of the diffusion equation, which in our present formalism, is represented by the time dependence of the capacity of the equivalent conductor, a simplification which results from the fact that the lowest eigenfunction describes the location of all except a fraction $\sim C_\alpha^2/R^2$ of the point defects.

VIII. DISLOCATIONS

The diffusion of point defects to dislocations has been studied by Koehler, Seitz, and Bauerle³ in the approximation, appropriate to low defect concentrations, that the climb is negligible. In this section we consider the modifications of the annealing characteristics introduced by the presence of climb.

The eigenfunctions of the diffusion equation which are appropriate to the problem of an infinitely extended linear sink in a cylindrical region of radius R are the

¹² H. Buchholz, *Elektrische und Magnetische Potentialfelder* (Springer-Verlag, Berlin, 1957).

cylinder functions

$$p_{lm}(\alpha_{lm}r_n) = \mathcal{C}_l(\alpha_{lm}r_n) \frac{\sin l\theta}{\cos l\theta} \quad (33)$$

which satisfy zero derivative boundary conditions at $r=R$, and in accordance with the discussion of Sec. III, go to zero at a radius $r=d$ of roughly atomic dimensions. This latter condition is not critical to the discussion since the eigenvalues are not sensitive to d , as, for example,⁷ is indicated in the case of the smallest eigenvalue:

$$\alpha_{01}^2 = 2R^{-2} \{ \ln R/d - 3/5 \}^{-1}. \quad (34)$$

For an initially uniform distribution of point defects, $\beta_{lm}(0) = 0$ for $l \neq 0$ [cf. Eq. (18)] and the lowest-order eigenfunction describes the location of just over half the defects, $p_{02}(\alpha_{02}r_n, \theta)$ about 10%, etc. The value of α_{02} is about $10\alpha_{01}$ so that in the absence of climb, almost half the defects anneal out in a time of $(\alpha_{02}^2 D)^{-1}$. The existing quenching techniques are not fast enough to retain an appreciable proportion of these transients, so that a simple exponential annealing of about half original defect concentration is expected to result from a fast quench.

In order to see the general effects of including climb in the analysis, we note that the time $(\alpha_{02}^2 D)^{-1}$ with $\alpha_{02} \approx 5/R$ corresponds to a random walk of the order of $R/5$. Now if the transients cause a climb of a distance greater than $R/5$, the transient components are replenished at the expense of the principal component $p_{01}(\alpha_{10}r_n, t)$ so that the transient annealing is extended. Evidently the criterion for the termination of transient annealing is

$$\bar{p} \gtrsim r_0 N_d^{1/2} / 2, \quad (35)$$

with \bar{p} the average occupation probability of a defect site, r_0 the atomic radius, and N_d the dislocation density. Equation (35) follows directly from the total dislocation climb

$$\zeta_0 \approx p_0 R / r_0 N_d^{1/2}, \quad (36)$$

which results from an initial occupation probability of p_0 , together with the maximum transient random walk distance of $R/5$. Since the transient absorption starts at a rate, given roughly by the Damask and Dienes estimate as about a factor 10^2 greater than that due to the principal component, it is evident that in the absence of cottering and pinning of dislocations, it would be difficult to quench into a specimen a quantity of defects greater than that given by Eq. (35).

It is interesting to consider in greater detail the quenching of samples under circumstances where the onset of this protracted transient behavior becomes important. To do this we consider the dislocation to carry along with its climb the region of radius R in which we are considering the kinetics subject to a zero derivative condition at R , the latter being an averaging device which permits us to estimate the annealing rate in terms of time independent eigenvalues.

The coupling terms on the right of Eq. (28) are readily evaluated by means of the addition relationship for cylinder functions,

$$|\mathbf{r} + \boldsymbol{\zeta}|^{-n/2} \mathcal{C}_n(|\mathbf{r} + \boldsymbol{\zeta}|) = \sqrt{2} \pi (r\zeta)^{-n} \sum_m (n+m) \mathcal{C}_{n+m}(r) \times J_{n+m}(\zeta) T_m^{n-1/2}(\cos\theta) \quad (37)$$

which in the case of the $l=0$ eigenfunctions gives

$$\partial p_{0m} / \partial \zeta = \alpha_{0m} \mathcal{C}_1(\alpha_{0m} r) \cos\theta \quad (38)$$

with $\cos\theta = \mathbf{r} \cdot \boldsymbol{\zeta} / r\zeta$. The p_{0m} therefore couple only to the p_{1n} , showing, as discussed above, that the deviations from simple annealing are due to the asymmetry of the defect distribution round the dislocation caused by the climb. While the p_{1n} components contain no defects; i.e.,

$$\sum_i p_{1n}(\mathbf{r}_i) = 0,$$

and therefore do not directly influence the annealing, they couple the p_{0m} together and thus cause an increased absorption rate indirectly.

It is helpful to note that the smallest antisymmetric eigenvalue, α_{11} , is considerably smaller than α_{20} , being about $4\alpha_{01}$ for typical dislocation densities, while the larger eigenvalues α_{0n} with $n > 1$ all correspond to faster decays than α_{02} . It is therefore to be anticipated that deviations from simple exponential annealing behavior will, in the low point-defect density limit, first become apparent because of a nonzero value of $\beta_{11}(t)$ after the quench. We therefore use the approximation $\beta_{lm}(t) = 0$, $l \neq 0$ except for $\beta_{11}(t)$. The equation describing $\beta_{11}(t)$ is then

$$d\beta_{11}/dt = -\alpha_{11}^2 D(t) [\beta_{11}(t) - \beta_{11}^0(t)] - \frac{d\zeta}{dt} \sum_l \beta_{0l}(t) \sum_n \frac{\partial p_{0l}(\mathbf{r}_n)}{\partial \zeta} p_{11}(\mathbf{r}_n). \quad (39)$$

During the quench, the symmetric transients anneal much more rapidly than $p_{11}(\mathbf{r}_n)$ so that the first term on the right of Eq. (39) is negligible. Moreover, on integrating Eq. (39), we note that the term on the right having the coefficient $\beta_{0l}(t)$ lasts only for a period $\tau_{0l} \sim (\alpha_{0l}^2 D)^{-1}$, and since both $\beta_{0l}(0)$ and τ_{0l} decrease very rapidly with increasing l , the series is well represented by its first term leaving the value of $\beta_{11}(\tau)$, with τ corresponding to the end of the transient phenomena, as

$$\beta_{11}(\tau) = - \int_0^\tau \frac{d\zeta}{dt} \beta_{01}(t) \sum_n \frac{\partial p_{01}(\mathbf{r}_n)}{\partial \zeta} p_{11}(\mathbf{r}_n) \quad (40)$$

$$\approx -\beta_{01}(0) \zeta_c \sum_n \frac{\partial p_{01}(\mathbf{r}_n)}{\partial \zeta} p_{11}(\mathbf{r}_n) \quad (41)$$

since $\beta_{01}(t)$ changes only slightly during a fast quench. Here ζ_c is the climb which occurs during the transient

annealing. It may be noted that Eq. (41) may be reproduced simply by considering the transients to be unaffected by the climb, and on the completion of transient annealing reanalyzing the remainder, namely, $\beta_{01}(t)p_{01}(\mathbf{r}_n)$, about the position ζ_i to which the dislocation has climbed.

When the transients are completed, which may effectively be quite early in the quench, the rapid climb ceases and $\beta_{11}(t)$ relaxes from the value $\beta_{11}(\tau)$ towards a much smaller value appropriate to the new climb rate, with the first term on the right of Eq. (39) dominant. For a quench ending at $t=\tau'$, both $\beta_{01}(t)$ and $\beta_{11}(t)$ obey an equation of the form

$$d\beta_\gamma/dt = \alpha_\gamma^2 D(t)\beta_\gamma \quad (42)$$

and therefore the value of $\beta_{11}(\tau')$ is given by

$$\frac{[\beta_{01}(\tau)]^{\alpha_{11}^2/\alpha_{10}^2}}{\beta_{01}(\tau')} = \frac{\beta_{11}(\tau)}{\beta_{11}(\tau')} \quad (43)$$

If δ is the small fractional loss of $\beta_{01}(t)$ during the whole quench, a lower limit on the value of $\beta_{11}(\tau')$ is therefore

$$\beta_{11}(\tau') = \beta_{11}(\tau) \exp[-\alpha_{11}^2 \delta / \alpha_{10}^2], \quad (44)$$

so that

$$\begin{aligned} \beta_{11}(t) = & -\beta_{01}(0)\zeta_i \exp[-\alpha_{11}^2 \delta / \alpha_{10}^2] \\ & \times \exp[-\alpha_{11}^2 D t] \sum_n \frac{\partial p_{01}(\mathbf{r}_n)}{\partial \zeta} p_{11}(\mathbf{r}_n) \end{aligned} \quad (45)$$

describes the behavior of $\beta_{11}(t)$ during the post-quench annealing when the climb rate is small.

Equation (45) may now be substituted into the equation

$$\frac{d\beta_{01}(t)}{dt} = -\alpha_{01}^2 D \beta_{01}(t) - \frac{d\zeta}{dt} \beta_{11}(t) \sum_n \frac{\partial p_{11}(\mathbf{r}_n)}{\partial \zeta} p_{01}(\mathbf{r}_n) \quad (46)$$

for the thermal excess of the component $p_{01}(\mathbf{r}_n)$, and using

$$\frac{d\zeta}{dt} = \frac{-\zeta_a}{\beta_{01}(\tau')} \frac{\partial \beta_{01}(t)}{\partial t} \quad (47)$$

together with the second of Eqs. (19) we finally obtain

$$\begin{aligned} d\beta_{01}(t)/dt = & -\alpha_{01}^2 \beta_{01} D / \{1 - \zeta_0^2 I^2 / 4 \\ & \times \exp[-\alpha_{11}^2 \delta / \alpha_{01}^2] \exp[-\alpha_{11}^2 D t]\}. \end{aligned} \quad (48)$$

To obtain Eq. (48) we have made the approximation $\zeta_a \zeta_i = \zeta_0^2 / 4$ where $\zeta_a = \zeta_0 - \zeta_i$ is the climb during the post transient anneal, the approximation being valid owing to the near equality of the number of defects contained respectively in the transient and in the principal annealing distributions. In Eq. (48) the symbol I which represents the sum over n in Eq. (46) is readily evaluated to give the magnitude $\sim 3/2R$ for typical dislocation densities.

Equation (48) is seen to predict infinitely fast annealing rates for the state of the annealing after quenching when $\zeta_0^2 I^2 / 4 \exp[-\alpha_{11}^2 \delta / \alpha_{01}^2] = 1$, a phenomenon which is symptomatic of the protracted transient annealing discussed in the early part of this section. With the value of I quoted above, and small fractional annealing δ of $p_{01}(\mathbf{r}_n)$ during the quench, this criterion may be written $\zeta_0/R \sim 1$ which is very close to the estimate obtained from Eqs. (35) and (36). For small point-defect concentrations Eq. (48) indicates that a transient of magnitude $\sim \zeta_0^2/R^2$ and duration $(\alpha_{11}^2 D)^{-1}$ may be expected as a consequence of the dislocation climbing into regions of the lattice which are still heavily populated with defects.

In summary, one can say that this analysis has shown that unless the defect concentration is large enough for the climb to be of the order of magnitude of the dislocation separation, the climb does not affect the annealing appreciably. When the climb is larger than this magnitude, it becomes difficult to quench into the samples concentrations of defects greater than that given by Eq. (35) unless clogging or pinning occurs. With $\bar{p} = 10^{-4}$ for $N_d \sim 10^8$ these conditions may in any event become difficult to achieve in practice, the more so since as in the case of gold, the tendency at high point-defect densities is for new and different types of sink to be nucleated.

IX. VOIDS

The kinetics of void growth by vacancy condensation may be obtained from the treatment by Ham of the analogous topic of precipitation in alloys. The nucleation of voids, either by precipitation on impurity sites or as a natural consequence of the interaction between vacancies, is a complex problem which we do not discuss in this treatment of monodefect kinetics. Instead we investigate the stability of voids against annihilation in favor of other sinks, a problem which may be studied without admitting an interaction between individual point defects.

In the cases of crystal boundaries, and perhaps dislocations, the energy of the extended defect is not changed on the average by the absorption of a vacancy. On the other hand, a void possesses a surface energy which is a function of the void size and therefore depends on the number of vacancies contained in the void. This fact results in an instability of the void in the presence of other sinks.

If we represent by σ the specific surface energy of the lattice, then for a void of radius b , the rate of energy change with volume is

$$dE/dV = 2\sigma/b \quad (49)$$

so that the average excess change in energy of the lattice on absorption of a vacancy is

$$\delta E_F = 8\pi\sigma r_0^3/3b. \quad (50)$$

We may simulate the resulting instability by considering the void as a region in which exists an excess δp over the thermal equilibrium occupation probability p_0 of a lattice site, which is given by

$$\delta p = 8\pi\sigma r_0^3 p_0 / bKT. \quad (51)$$

Let us first examine the stability of a set of voids of different sizes in the absence of other sinks. To do this we construct a lattice of voids having radii b_1 and b_2 on alternate sites of a sodium chloride structure, with excess vacancy concentrations inside the alternate voids of δp_1 and δp_2 , respectively. The boundary conditions imposed on the diffusion equation are that $p = \delta p_1$ at b_1 and $p = \delta p_2$ at b_2 , and moreover, we know that the fluxes of vacancies out of neighboring cells should be equal and opposite. In a Wigner-Seitz type approximation, the latter condition may be interpreted as a need for the radial derivative of the occupation probability to be equal and opposite at the boundaries of adjacent cells. To the order of b/R , this condition leads to the same eigenvalue of the diffusion equation as that found with a zero derivative at the cell boundary, namely $(3b_1/R^3)^{1/2}$ for a cell containing a void of radius b . The average occupation probability \bar{p} of defect sites in the lattice is then

$$\bar{p} = [1 + 16\pi\sigma r_0^3 / 3kT(b_1 + b_2)] p_0 \quad (52)$$

and the flux flowing from smaller to larger voids is

$$\frac{dN}{dt} = \frac{8\pi\sigma D_i (b_1 - b_2)}{kT (b_1 + b_2)}, \quad (53)$$

where $D_i = p_0 D$, the diffusion coefficient of the ions in the lattice. For gold, with $\sigma_0 \sim 10^3$ ergs cm^{-2} , even at 300°C the predicted flux is of the order of hundreds of vacancies per second between voids of radii differing by a factor of two, so that the smaller voids are annihilated at relatively low temperatures.

The rate of emission of vacancies from a void is proportional to the difference between the occupation probability $p_0 + \delta p$ in the lattice surrounding the void, and the probability $p_0 + \delta p'$ with which the voids would be in thermal equilibrium:

$$\partial N / \partial t = 3bD(\delta p' - \delta p)r_0^{-3}. \quad (54)$$

This makes possible a simple estimate of void stability in the presence of sinks whose energy is not dependent on their defect content, for the diffusion equation for the thermal excess of vacancies then assumed the form

$$D\nabla^2 \delta p = \partial(\delta p) / \partial t + 4\pi b D N_V (\delta p - \delta p'), \quad (55)$$

where N_V is the void concentration and the voids have all been given the same radius b . In the quasisteady state in which the voids emit and the sink absorbs, we may ignore the time derivative leaving

$$\nabla^2 s = 4\pi b N_V s \quad (56)$$

to be solved subject to $s = \delta p - \delta p' = 0$ at the sinks. In the case of dislocations, the appropriate solution of Eq. (56) is

$$\delta p(r) = \delta p' [1 - K_0(\gamma r) / K_0(\gamma d)], \quad (57)$$

with $\gamma = (4\pi N_V b)^{1/2}$ and K_0 a modified Bessel function of the second kind, the modified function of the first kind playing a minor role for well-separated dislocations. The vacancy absorption rate at the dislocation is then given by

$$\partial N / \partial t = - (4\pi\sigma D_i / kTb) / \ln(\pi N_V b d^2)^{1/2}, \quad (58)$$

where d is the dislocation "radius." However, this estimate is not very satisfactory since, as the voids near the dislocation decrease in size, they will become increasingly unstable so that the dislocation will annihilate the neighboring voids first and in this way make a hole of gradually increasing radius in the void distribution. Owing to the increased instability of voids near the dislocation, the voids remote from the sink may even grow during the early stages of the annealing.

X. CONCLUSION

We have shown that the diffusion equation is a good approximation for studies of point-defect annealing kinetics even when the sinks to which the defects anneal are of atomic dimensions. The boundary condition to be applied to solutions of the diffusion equation have been elucidated in terms of the difference equation to which the differential diffusion equation is a macroscopic approximation. Only for very small sinks do these boundary conditions differ appreciably from the macroscopic condition of zero excess concentration at the sink sites.

The development of equations which describe diffusion in the presence of time dependent sink properties, together with the electrostatic approximation to the diffusion equation, have allowed us to study the annealing of point defects to stacking-fault tetrahedra, to dislocation loops, and to climbing dislocations. We have also considered the problem of void stability in the presence of other sinks.

The discussions given in this article have been subject to the assumption that the defect jumps in the good crystal are reversible, with jump times the same at either end of any jump path. In this way we have excluded interactions both between the point defects themselves and between the defects and the sinks. The former consequence is not important for low point-defect concentrations, but the latter may modify the annealing characteristics considerably, particularly in cases involving dislocations, where the long range strain field associated with the sinks may invalidate the condition $\tau_{ni} = \tau_{in}$ over a large proportion of the lattice. A reliable extension of the theory to include the long-range elastic interaction between point defects and sinks, and

the short-range electronic interaction between the defects themselves, is therefore needed to further the present understanding of defect kinetics.

Finally, we note that the description of defects annealing to sinks is more easily achieved than that of the production of point defects by sinks, for while jumps into the sink may be well represented on the average by the jump time formalism, certain jumps of point defects out of sinks which are involved in breaking down sink geometries of high symmetry may well be constrained by other energetic considerations. The abrupt decay of stacking-fault tetrahedra at temperatures above 600°C is an example of this type of process

in which the diffusion from the sink is limited by a surface reaction at the sink. It seems reasonable to assume that vacancy production of crystal boundaries other than those parallel to atomic planes, and at the surfaces of voids, is not restrained in this fashion.

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Dynamics of Radiation Damage in a Body-Centered Cubic Lattice*

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Radiation damage has been studied by numerically integrating the equations of motion of a large set of atoms on a high-speed computer. In this paper the method is applied to a model of α iron. Low energy events have been extensively investigated. The primary knock-on atom is found to initiate an extended sequence of correlated replacements, producing an interstitial at some distance and a vacancy on its original site. The interstitial is found to have a split configuration, as was found earlier in copper, but its axis lies along $\langle 110 \rangle$. Collision chains are found to be prominent in $\langle 111 \rangle$ and $\langle 100 \rangle$, and attenuation rates and focusing parameters for these chains are determined. The threshold energy for displacing an atom is found to be highly dependent on the direction of the knock-on. The lowest threshold is found to be 17 eV, for knock-ons directed near $\langle 100 \rangle$, and to be about 34 eV and 38 eV for those directed near $\langle 110 \rangle$ and $\langle 111 \rangle$, respectively. The probability of displacement for a randomly directed knock-on of energy E is determined for E between 0 and 60 eV. The results are in approximate agreement with experiments of Lucasson and Walker, although more structure is found in the calculated curve than could be tested by the experiments. Pronounced directional effects in low energy electron bombardments of α iron single crystals are predicted.

1. INTRODUCTION

THE processes by which radiation damage is produced in a crystal have recently been investigated by a new method in which the classical equations of motion of a set of several hundred to a thousand atoms are integrated on a high-speed computer. The atoms are allowed to interact with fairly realistic central forces augmented by special forces on the atoms at the edge of the set designed to simulate the influence of surrounding material. Initially the atoms are at rest on the sites of a perfect lattice, and the start of a radiation damage event is considered to be the sudden transfer of momentum to one of the atoms (the primary knock-on) by an irradiating particle. The primary knock-on then energizes other atoms in a complex many-body process, and when the agitation dies away the model crystallite is left in a damaged state. Since the primary knock-on may have any momentum, within wide limits, a series of calculations for representative initial condi-

tions must be made. No presuppositions about the nature of the lattice defects or about thresholds for their production are made—such information is an end product of the calculations. The chief assumption which must be made is the form of the interatomic potential energy, and a number of experimental and theoretical requirements are imposed. Also, an upper limit on the energy of the primary knock-on is imposed by the size of the set of atoms.

The first calculations of this kind were made on a model representing copper.¹⁻⁷ A large number of calcu-

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