

Thermal Equilibrium Kinetics of Interacting Point Defects*

C. P. FLYNN

Department of Physics, University of Illinois, Urbana, Illinois

(Received 28 October 1963)

The local kinetics of an interacting defect species is treated on the assumption that local thermal equilibrium prevails, and a thermal equilibrium diffusion coefficient appropriate to any locality is derived in its general form. The annealing of an interacting defect species to sinks in the lattice is then shown to be identical with that of noninteracting defects having a diffusion coefficient

$$D_{\text{eff}} = \sum_{n\alpha} n c_{n\alpha}^0 D_{n\alpha} / \sum_{n\alpha} n c_{n\alpha}^0,$$

where $c_{n\alpha}^0$ is the concentration far from the sink of an n th order cluster of type α , and $D_{n\alpha}$ is its diffusion coefficient. The importance of the particular case when $c_{n\alpha}^0$ achieves the thermal equilibrium value $c_{n\alpha}^t$, is noted, and the range of applicability of this diffusion coefficient is discussed.

I. INTRODUCTION

THE theoretical description of the annealing of a single species of defects out of a crystal lattice is considerably complicated by the inclusion of an interaction between the defects. For the case of noninteracting defects in an unstrained lattice, it can be shown¹ that the diffusion equation

$$\nabla \cdot \mathbf{D} \cdot \nabla p(\mathbf{r}, t) = \partial p(\mathbf{r}, t) / \partial t, \quad (1)$$

with \mathbf{D} the diffusion tensor of the perfect lattice, and $p(\mathbf{r}, t)$ the probability of occupation of a potential defect site at \mathbf{r}, t always gives a good description of the annealing process. Since the defects do not interact, \mathbf{D} is a constant throughout the good lattice. The diffusion equation may therefore, in principle, be solved subject to reasonable boundary conditions at the sites of efflux of the defects from the good lattice by means of an eigenfunction expansion of $p(\mathbf{r}, t)$ in the form

$$p(\mathbf{r}, t) = \sum_n \alpha_n p_n(\mathbf{r}) \exp(-\lambda_n t). \quad (2)$$

When an interaction between the defects is introduced, Eq. (1) with a constant \mathbf{D} fails to give an accurate account of the kinetics, because the interaction forces cause local modifications of the diffusion coefficient which may result in radical changes in mobility of the defects in the lattice. This is particularly the case when an appreciable number of defects become tightly bound into clusters whose migration rate is significantly different from that of the individual defects. Recognition of this type of behavior has led to attempts to describe the kinetics in terms of a diffusion coefficient for the individual clusters and the relative proportions of the various clusters present. Thus, Koehler, Seitz, and Bauerle² noted that in quenched Au, the vacancies spend a time τ_2 paired into divacancies, as compared with τ_1 in the form of monovacancies, and therefore the effective diffusion coefficient of the

defects is expected to have the form

$$D = (\tau_1 D_1 + \tau_2 D_2) / (\tau_1 + \tau_2). \quad (3)$$

Here, D_1 and D_2 are the diffusion coefficients of monovacancies and divacancies, respectively, as defined for cubic lattices by the relationship

$$dN_\alpha/dt = D_\alpha \int_s \text{grad} c_\alpha \cdot ds, \quad (4)$$

where the left-hand side represents the rate of passage of defects α through the surface s in the presence of the concentration distribution $c_\alpha(\mathbf{r})$.

One may note in passing that for complexes the definition of the diffusion coefficient by means of Eq. (4) is only meaningful when coupled with a thermal equilibrium postulate, because the possible jumps of the complex will not, in general, possess the lattice symmetry. This symmetry is only obtained on averaging the properties of the complex over the various rotations appropriate to the lattice symmetry, and is lost by the translational diffusion in a concentration gradient unless mechanisms operate to restore the local equality of the population of different rotational isomers of the complex. A further difficulty in defining the diffusion coefficient of complexes springs from the fact that the configuration of all complexes of order $n > 1$, other than fcc divacancy, is changed by some of the possible diffusion jumps of its constituent defects. However, one may still define a diffusion coefficient for each configuration of a complex of a given order making use of the lattice symmetry and the thermal equilibrium postulate mentioned above, together with random flight arguments. In what follows we will specify by $D_{n\alpha}$ and $c_{n\alpha}(\mathbf{r})$ the diffusion coefficient defined in this way, and the local concentration of a particular configuration α of an n th-order cluster.

The concept of local thermal equilibrium is of further importance in one approach to the kinetics of systems of interacting defects which we will adopt here, for the determination of the local population of various complexes by the thermal equilibrium conditions results in

* Supported in part by the U. S. Atomic Energy Commission.

¹ C. P. Flynn, Phys. Rev. **133**, 587 (1964).

² J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

a coupling of the gradients under which the different complexes diffuse. It has been remarked by de Jong and Koehler³ that this coupling helps to modify the diffusion coefficient given by Eq. (3) into the form

$$D = (D_1\tau_1 + 4D_2\tau_2) / (\tau_1 + 4\tau_2), \quad (5)$$

where the factor 4 is attributed in part to the coupling of the gradients, and in part to the greater mass transport produced by motion of the divacancy.

The diffusion coefficients given in Eq. (5) is not yet of the correct form for describing the diffusion of vacancies and divacancies to sinks, for Eq. (5) gives a local concentration-dependent diffusion coefficient, and takes no account of the range of concentrations throughout a lattice necessary to produce the gradients which drive the diffusion. Thus, the excess defect density outside the sinks falls to zero at the sink surface. One may note in this respect that in relatively low-temperature annealing experiments, where the equilibrium concentration of divacancies may be negligible, the consequence of equilibration during migration is that the divacancies can never reach the sink whatever their actual concentration in the lattice. In this way the spatial variation in defect concentration can cause a dependence of diffusion coefficient on position which must be taken into account in finding the net defect flux to the sinks.

In what follows, we will first derive the general form of the local thermal equilibrium diffusion coefficient. It is then shown that regardless of the degree of equilibrium present, an almost exact solution of the kinetics of the interacting defects may be found for the description of annealing to localized sinks. The range of validity of the particular solution found by assuming that thermal equilibrium occurs in the lattice is then discussed.

II. LOCAL DIFFUSION IN THERMAL EQUILIBRIUM

Let us suppose that in the defect species to be studied, the defects interact in a relatively short-ranged fashion, or are at a sufficiently low density in the crystal that we can divide the defect population into clusters inside which the defects interact, but without interactions occurring between one cluster and its neighbors. Further, we will postulate that the concentrations of the different complexes present in a locality of the lattice are those given by the thermal equilibrium condition. This second assumption ensures that while the total concentration $c(\mathbf{r})$ of defects in the lattice may depend on position, the proportions of the various clusters at \mathbf{r} depends only on $c(\mathbf{r})$.

With n and α specifying the order and configuration of a cluster as before, we may write

$$c(\mathbf{r}) = \sum_{n,\alpha} n c_{n\alpha}(\mathbf{r}), \quad (6)$$

where the summation extends over all configurations of all orders of cluster present. It has been shown by Brooks⁴ that for a fixed defect concentration in thermal equilibrium in a given region

$$c_{n\alpha}(\mathbf{r}) = \beta_{n\alpha} c_1^n(\mathbf{r}), \quad (7)$$

where $c_1(\mathbf{r})$ is the concentration of single defects at \mathbf{r} (the subscript α may be omitted in this instance) and $\beta_{n\alpha}$ is given by

$$\beta_{n\alpha} = \gamma_{n\alpha} \exp(-B_{n\alpha}/kT), \quad (8)$$

where $B_{n\alpha}$ is the energy loss of the lattice on forming the complex from isolated defects, $\gamma_{n\alpha}$ is a configurational factor, and k and T have their customary significance. One may therefore rewrite Eq. (6) in the form

$$c(\mathbf{r}) = \sum_{n\alpha} n \beta_{n\alpha} c_1^n(\mathbf{r}). \quad (9)$$

From differentiation of Eq. (7), it is found that

$$c_{n\alpha}^{-1}(\mathbf{r}) \mathbf{grad} c_{n\alpha}(\mathbf{r}) = n c_1^{-1}(\mathbf{r}) \mathbf{grad} c_1(\mathbf{r}), \quad (10)$$

so that the relative equilibrium gradients under which the clusters of different orders diffuse are proportional to their order. By definition, the number of defects passing through a surface s in unit time is given by

$$\begin{aligned} \frac{dN}{dt} &= \sum_{n\alpha} n D_{n\alpha} \int_s \mathbf{grad} c_{n\alpha}(\mathbf{r}) \cdot \mathbf{ds} \\ &= c_1^{-1}(\mathbf{r}) \sum_{n\alpha} n^2 c_{n\alpha}(\mathbf{r}) D_{n\alpha} \int_s \mathbf{grad} c_1(\mathbf{r}) \cdot \mathbf{ds} \end{aligned} \quad (11)$$

from Eq. (10). The local thermal equilibrium diffusion coefficient is defined by

$$\begin{aligned} \frac{dN}{dt} &= D \int_s \mathbf{grad} c(\mathbf{r}) \cdot \mathbf{ds} \\ &= D c_1^{-1}(\mathbf{r}) \sum_{n\alpha} n^2 c_{n\alpha}(\mathbf{r}) \int_s \mathbf{grad} c_1(\mathbf{r}) \cdot \mathbf{ds}, \end{aligned} \quad (12)$$

where use has been made of Eqs. (7) and (9). By comparison of Eqs. (11) and (12) one finally obtains the local diffusion coefficient

$$D(\mathbf{r}) = \sum_{n\alpha} n^2 c_{n\alpha}(\mathbf{r}) D_{n\alpha} / \sum_{n\alpha} n^2 c_{n\alpha}(\mathbf{r}). \quad (13)$$

Within the restriction to local equilibrium kinetics, Eq. (13) should be of quite general application. Thus, in the case of equilibrium between single and paired defects, one finds

$$D(\mathbf{r}) = (c_1 D_1 + 4c_2 D_2) / (c_1 + 4c_2). \quad (14)$$

³ M. de Jong and J. S. Koehler, Phys. Rev. **129**, 49 (1963).

⁴ H. Brooks, in *Impurities and Imperfections* (American Society for Metals, Cleveland, Ohio, 1955), pp. 1-27.

III. DIFFUSION TO SPHERICAL SINKS

Having obtained an expression for the local annealing behavior of the clusters, one may now write down the diffusion equation describing the migration process to the sinks:

$$\nabla \cdot D(\mathbf{r}) \nabla c(\mathbf{r}) = \partial c(\mathbf{r}) / \partial t. \quad (15)$$

Equation (15) must be solved subject to the usual boundary condition of zero excess concentration above the thermal equilibrium value at sink sites. Unfortunately, the equation is nonlinear in c for values of c such that $D \neq D_1$, so that the standard procedures used in linear diffusion problems are not available here. However, the solution of the linear problem does suggest an approach which is valuable in the nonlinear case also.

It will be recalled that with a constant diffusion coefficient and for localized sinks (dislocation loops, clusters, stacking fault tetrahedra, and the like) which are randomly dispersed through the good crystal, we first assign to each sink a volume from which the defects are likely to anneal to that sink. On idealizing the problem with the supposition that these volumes, and the position of the sink in the volume, have some convenient geometry, the annealing problem may be simulated by solving the diffusion equation inside the individual cell, subject to zero derivative conditions at the surface and zero concentration at the sink. For a uniform initial distribution of defects at concentration c_0 , and concentric spherical sinks, radius b , and diffusion volumes, radius R , one finds in this way⁵

$$c(r, t) = \sum_n a_n (\lambda_n r)^{-1} \sin \lambda_n (r - b) \exp(-\lambda_n^2 D t), \quad (16)$$

where λ_n is the n th root of the equation

$$\tan \lambda_n (R - b) = \lambda_n R. \quad (17)$$

The interesting point concerning this solution is that the eigenvalue corresponding to the smallest eigenvalue λ_0 describes the annealing of all except a fraction $\sim b^2/R^2$ of the defects and, moreover, that the defect absorption rate found from use of this eigenvalue alone differs only by $\sim b^2/R^2$ from the steady-state rate of absorption from an infinite diffusion field. The net contribution of the eigenfunctions for $n > 0$ is a small transient whose amplitude is negligible for $b \ll R$. Thus, in practice, to find the defect loss rate at a spherical sink, we need only solve Laplace's equation

$$\nabla^2 c(\mathbf{r}) = 0 \quad (18)$$

and knowing the diffusion coefficient, the defect loss rate may be written down from the concentration gradient at the sink.

The reason for this simplification rests on the fact that the great majority of defects reaching the sink have to migrate from the outer parts of the diffusion volume. Compared to the rate at which defects reach the sink, the rate of change of the average number of defects near

the sink is very small, and a close approximation to steady-state conditions is the consequence. However, this is also true in the case where the diffusion equation varies with position: The majority of the defects lie initially at distances $\sim R$ from the sink, so that quasi-steady-state conditions will prevail. Thus, the nonlinear problem also may be solved to a good approximation by determining the solution of

$$\nabla \cdot D(\mathbf{r}) \nabla c(\mathbf{r}) = 0 \quad (19)$$

for diffusion out of an infinite volume.

Fortunately, Eq. (19) is quite easy to solve for the case of spherical symmetry. Noting that according to the thermal equilibrium conditions, $D(\mathbf{r})$ is actually a function of concentration only, we may immediately integrate the equation twice to obtain

$$a_1 + a_2/r = \int D(c) dc, \quad (20)$$

where a_1 and a_2 are constants of integration. On changing the variable to c_1 one finds

$$\begin{aligned} a_1 + \frac{a_2}{r} &= \int c_1^{-1} \sum_{n\alpha} n^2 c_{n\alpha} D_{n\alpha} dc_1 \\ &= \sum_{n\alpha} n c_{n\alpha} D_{n\alpha}, \end{aligned} \quad (21)$$

where use has again been made of Eqs. (6) and (7).

The arguments given above show that Eq. (21) holds provided that thermal equilibrium exists throughout the lattice, but as we will now demonstrate, its range of validity is, in fact, much wider. The exact description of the annealing behavior of an interacting defect species is available from the coupled set of partial differential equations which give the time dependence of the concentrations of the various clusters (see, for example, Ref. 3):

$$D_{n\alpha} \nabla^2 c_{n\alpha} + \varphi_{n\alpha}(c_1, c_{2\beta}, \dots, c_{n\beta}, \dots) = \partial c_{n\alpha} / \partial t, \quad (22)$$

where the different equations are generated by running n and α over all orders and types of complexes present. The function $\varphi(c)$ describes the rate of change of $c_{n\alpha}(\mathbf{r})$ due to transformations among the clusters.

On multiplying each of Eqs. (22) by its order n and adding the whole set together, one finds after trivial manipulations

$$\nabla^2 \sum_{n\alpha} n c_{n\alpha} D_{n\alpha} + \sum_{n\alpha} n \varphi_{n\alpha}(c_1, c_{2\beta}, \dots, c_{n\beta}, \dots) = \partial c / \partial t. \quad (23)$$

Here we have made the obvious identification $c = \sum_{n\alpha} n c_{n\alpha}$. The second term on the left vanishes, since no defects are created by means of the transformations between clusters; moreover, in the quasisteady

⁵ F. S. Ham, Phys. Chem. Solids **6**, 335 (1958).

state, the right-hand side also vanishes. Thus, we have

$$\nabla^2 \sum_{n\alpha} n c_{n\alpha} D_{n\alpha} = 0. \quad (24)$$

On integrating twice, Eq. (21) is reproduced for the case of spherical symmetry, although more generally, since the $c_{n\alpha}$ are no longer restricted to thermal equilibrium proportions.

The constants of integration are readily evaluated from the conditions

$$c_{n\alpha} = 0, \quad \text{at } r = b \quad (25a)$$

$$c_{n\alpha} = c_{n\alpha}^0, \quad c = c_0, \quad \text{at } t = \infty \quad (25b)$$

where $c_{n\alpha}^0$ is the concentration of the complex n, α as c tends to its maximum value c_0 . In this way, one finds the values

$$a_1 = a_2/b = \sum_{n\alpha} n c_{n\alpha}^0 D_{n\alpha}, \quad (26)$$

and therefore

$$\sum_{n\alpha} n c_{n\alpha}(r) D_{n\alpha} = (1 - b/r) \sum_{n\alpha} n c_{n\alpha}^0 D_{n\alpha}. \quad (27)$$

By taking the radial derivative at $r=b$ and integrating over the surface of the sink, the number of defects entering the sink in unit time is found as

$$\frac{dN}{dt} = 4\pi b \sum_{n\alpha} n c_{n\alpha}^0 D_{n\alpha}. \quad (28)$$

Rather surprisingly, this is just the defect loss rate which would be found if concentrations $c_{n\alpha}^0$ of defects were allowed to diffuse without interactions.

The effective diffusion coefficient D_{eff} may be defined from analogy with the relationship similar to Eq. (28) which is found when the diffusion equation is a constant, namely,

$$dN/dt = 4\pi b c_0 D_{\text{eff}}. \quad (29)$$

Comparing Eqs. (24) and (25), one then finds

$$D_{\text{eff}} = c_0^{-1} \sum_{n\alpha} n c_{n\alpha}^0 D_{n\alpha}, \quad (30)$$

or, substituting for c_0 ,

$$D_{\text{eff}} = \frac{\sum_{n\alpha} n c_{n\alpha}^0 D_{n\alpha}}{\sum_{n\alpha} n c_{n\alpha}^0}. \quad (31)$$

The diffusion coefficient given by Eq. (31) has been derived for spherical sinks only. In fact, the range of validity is wider, as will be discussed in the next section. For the special case of single and paired defects, one finds that the flux of defects to the sink is described by

$$D_{\text{eff}} = (c_1^0 D_1 + 2c_2^0 D_2) / (c_1^0 + 2c_2^0). \quad (32)$$

It is interesting to note that Eq. (27) defines the profile of the concentration of defects in the presence of the sink. Figure 1 shows the thermal equilibrium profile for three different concentrations of vacancies in Au at

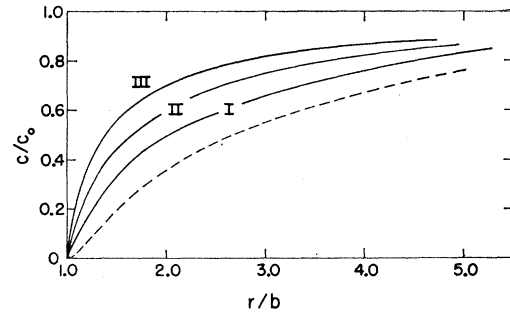


FIG. 1. Relative vacancy concentration c/c_0 near a localized sink of radius b in Au at 300°K for the following values of c_0 : (I) $c_0 \rightarrow 0$; (II) $c_0 = 2 \times 10^{-6}$; (III) $c_0 = 2 \times 10^{-4}$. The broken line shows the relative divacancy component c_2/c_2^0 for case II.

300°K. To obtain these distributions we have used the relationships

$$D_1 = \nu_1 a^2 \exp(-E_m^1/kT),$$

$$D_2 = (\nu_2 a^2/6) \exp(-E_m^2/kT), \quad (33)$$

and

$$c_2 = 6c_1^2 \exp(B/kT).$$

Equations (33) may be obtained from Ref. 3 (with the exception of the second equation where a factor 8 is given in place of the factor 6 found here from the type of random flight arguments mentioned in the Introduction). We have also used the values $\nu_1 = \nu_2$ and $E_m^1 - E_m^2 + B = 0.26$ eV.

From Fig. 1 it will be seen that, as the defect concentration increases, the profile tends away from that found with a constant diffusion coefficient in a manner which exaggerates the gradients near the sink. This is a consequence of the fact that the divacancies diffuse faster than the singles, so that the equilibrium profile has smaller gradients away from the sink where the concentration of divacancies is largest. Close to the sink where only single vacancies exist, the gradients are enhanced in order to maintain the increased quasi-steady-state flow.

IV. DIFFUSION TO NONSPHERICAL SINK GEOMETRIES

In general, a localized sink will not be spherical, so that the theory given above does not necessarily hold. In the case of a constant diffusion coefficient, it has been shown by Flynn¹ that the absorption rate of defects at a nonspherical sink is the same as that at a spherical sink whose radius equals the electrostatic capacity of a conductor having the dimensions of the nonspherical sink.

When the defects interact, this theorem retains its validity with an effective sink radius unchanged by the interactions. To prove this, we note that according to Eq. (24) the quantity $\sum_{n\alpha} n c_{n\alpha} D_{n\alpha}$ can be expanded in terms of the customary solutions $(A r^l + B r^{-l-1}) Y_{ln}(\theta, \varphi)$ of Laplace's equation. Differentiation then reveals that the coefficient B_0 alone determines the flux of defects

through a surface surrounding the sink, and comparison with the analogous electrostatic field shows that the value of B_0 corresponds to that of a spherical sink with a radius equal to the capacitance of the actual sink geometry. One may therefore write the defect annealing rate for any degree of equilibrium and any sink geometry in the form

$$dN/dt = 4\pi c_0 b_{\text{eff}} D_{\text{eff}} = 4\pi b_{\text{eff}} \sum_{n\alpha} n c_{n\alpha}^0 D_{n\alpha}, \quad (34)$$

with D_{eff} given by Eq. (31) and b_{eff} by the electrostatic capacitance appropriate to the sink geometry.

It is interesting also to consider the case of sinks having cylindrical symmetry in an attempt to discuss diffusion to dislocations in the presence of interactions between the diffusing defects. We therefore solve Eq. (24) in cylindrical coordinates to obtain in place of Eq. (21)

$$a_1 + a_2 \ln r = \sum_{n\alpha} n c_{n\alpha} D_{n\alpha}. \quad (35)$$

Difficulty is encountered in applying the boundary conditions at large r because of the logarithmic divergence of the left-hand side of Eq. (31). However, comparison with the analogous equation when D is constant shows that for steady-state annealing, the effective diffusion coefficient is given once more by Eq. (31).

V. THE THERMAL EQUILIBRIUM APPROXIMATION

It is clear that the approximation of local thermal equilibrium is appropriate to small concentration gradients, for the migration is then slow, and the defect population has sufficient time to equilibrate during diffusion. For localized sinks, the gradients are largest near the sink, so that it is in this neighborhood that the approximation first breaks down. The migrating complexes have a lifetime and a mean path which are independent of their environment. Thus, the occurrence of local thermal equilibrium depends on the relative sizes of the mean path of the complexes, and the distance over which the concentration of the complexes must change significantly.

During annealing with a constant diffusion coefficient to localized sinks, radius b , the defect concentration essentially falls to zero in a distance $\sim b$ outside the sink. When interactions between defects are added so that the effective diffusion coefficient becomes D_{eff} rather than D_1 , the gradients close to the sink are increased by a factor D_{eff}/D_1 in order to accommodate the increased defect flux, and the concentration decrease therefore occurs in a distance $\sim D_1 b / D_{\text{eff}}$ (see Fig. 1). Given a mean path λ of the complexes, one then sees that the complexes cannot reach the sink if $D_1 b / D_{\text{eff}} \lambda \gg 1$ and that, under these circumstances, the thermal equilibrium conditions will effectively be satisfied throughout the lattice.

To exemplify the discussion, one may again consider the annealing of single and divacancies in Au at 300°K.

Using Eqs. (33) one finds

$$D_{\text{eff}} \lambda_2 / D_1 = \frac{1 + 24e^{B/kT} c_1 D_2 / D_1}{1 + 24e^{B/kT} c_1} [D_2 e^{B/kT} / 14 D_1]^{1/2} a, \\ = \frac{1 + 4c_1 \Delta(T)}{1 + 24e^{B/kT} c_1} [\Delta(T) / 112]^{1/2} a, \quad (36)$$

where

$$\Delta(T) = \exp[(E_m^1 - E_m^2 + B) / kT], \quad (37)$$

and we have written λ_2 for the mean divacancy path. $\Delta(T)$ has a value of about 3×10^4 for Au at 300°K, so that with $c_1 \lesssim 3 \times 10^{-4}$ thermal equilibrium conditions will be approached at all points for sinks with $b \gtrsim 300a$. For samples quenched from temperatures below 900°C, this criterion becomes $b \gtrsim 60a$. For Ag at room temperature, $e^{B/kT} \sim 10^6$, so that the second term in the denominator dominates for even moderate defect concentrations. One then finds $D_{\text{eff}} \lambda_2 / D_1 = [D_2^3 e^{B/kT} / 14 D_1^3]^{1/2} a$, which indicates that almost macroscopic sinks are needed in order to assure local thermal equilibrium everywhere. At around 900°C, however, the equilibrium in Ag adopts a form analogous to that in Au at room temperature.

It is important to note that the breakdown of thermal equilibrium near the sink does not affect the validity of the expressions (28) and (31) for the defect loss rate and effective diffusion coefficient, for these are quite generally applicable to the quasisteady state. However, in order to find the kinetics resulting from any given annealing situation, one needs also the value of the $c_{n\alpha}^0$, which must be furnished by further consideration of the boundary conditions of the problem. In the relatively wide range of circumstances where thermal equilibrium is attained in the bulk lattice, the solution is immediately available, for then the $c_{n\alpha}^0$ take their thermal equilibrium values $c_{n\alpha}^t$, which may be found from the concentration c of defects remaining in the lattice. The thermal equilibrium diffusion coefficient

$$D_{\text{eff}} = \sum_{n\alpha} n c_{n\alpha}^t D_{n\alpha} / \sum_{n\alpha} n c_{n\alpha}^t \quad (38)$$

then describes the annealing.

We will now examine the range of circumstances under which we may apply Eq. (37) to our relatively simple example of mixed single and divacancy annealing to an isolated sink. Because divacancies diffuse more rapidly than single vacancies, the thermal imbalance of the defect population which arises from steady-state annealing is always in the direction of a divacancy deficiency, the vacancies being unable to maintain the thermal equilibrium divacancy population in the face of rapid divacancy migration.

One can easily show that if the divacancy population is suppressed by δc_2 , then the local production rate resulting from the deviation from equilibrium is

$$dc_2/dt = 28\nu_1 \exp[-(E_m' + B) / kT] \delta_2. \quad (39)$$

Moreover, the loss rate due to migration may be seen from Eq. (28) to take the form

$$dc_2/dt = -(3b/R^3)D_2c_2, \quad (40)$$

so that for the approximate steady state

$$\delta c_2/c_2 \sim (ba^2/56R^3)\Delta(T). \quad (41)$$

This shows that for Au at 300°K with $5b=R$, a separation of the sinks by $50a$ is sufficient to ensure the validity of Eq. (37). For Ag at room temperature, the analogous distance is some thousands of lattice spacings.

Finally, it is interesting to re-examine the work of de Jong and Koehler³ in the light of what we have found here. These authors study the growth of stacking fault tetrahedra under the assumptions: (a) that growth occurs by absorption at the corners of the tetrahedra at a rate found by assuming that the defect concentration is constant through the lattice, and (b) that the diffusion coefficient for voids is the local thermal-equilibrium value corresponding to the average defect concentration. The assumption (a) has previously been shown by

the author¹ to lead, in general, to a quite incorrect estimate of the defect loss rate. However, when one specifies a single atomic site as an infinite sink, this approximation leads to an erroneous estimate by only about a factor 2, because the gradients driving such a slow diffusion process are indeed almost negligible. Since, in this isolated case, the occupation probability of a potential defect site does not fall to zero at sites neighboring the sink, the averaging process involved in finding Eq. (21) from Eq. (13) does not occur, and the diffusion coefficient (13) may therefore be more appropriate than (31). Thus, provided the defect absorption occurs in regions of atomic dimensions near the tetrahedron corners, the assumptions made by de Jong and Koehler could give a reasonable description of the annealing.

ACKNOWLEDGMENTS

The author is indebted to Professor R. W. Balluffi for discussions during which the wide range of applicability of D_{eff} emerged. He also wishes to thank Professor D. Lazarus and Professor J. S. Koehler for their helpful comments.

Effect of Long-Range Interactions on Order*

ARTHUR PASKIN

Brookhaven National Laboratory, Upton, New York

(Received 21 October 1963)

Harrison and Paskin (HP) have calculated the ordering energy of β -CuZn using recent theoretical techniques of treating electron screening and Mott's polar model of an alloy. Good agreement is obtained between the calculated total energy of the order-disorder transformation and specific-heat measurements. A consequence of the HP calculation is that the ordering energy is long-range and oscillates in sign. Walker and Keating recently measured the neutron diffuse scattering of β -CuZn above the critical temperature T_c and find their data are in agreement with order calculated by only considering a nearest-neighbor interaction. Using the Cowley statistical theory of order, we compare the order generated by a nearest-neighbor interaction and the long-range interaction of HP at a temperature $1.1T_c$. We find the average behavior of the order generated by the nearest-neighbor and long-range interaction to be similar. The major difference is the nearest-neighbor interaction generates order that asymptotically, varies smoothly with neighbor distance whereas the order resulting from the long-range interaction fluctuates markedly about the nearest-neighbor generated order. This result may explain the success of statistical theories, based on nearest-neighbor interactions, in both order-disorder of alloys as well as in some magnetic systems which are also believed to have a similar long-range oscillatory interaction.

INTRODUCTION

HARRISON and Paskin¹ (HP) have calculated the ordering energy of β -CuZn using recent theoretical techniques of treating electron screening² and Mott's³ "polar model" of an alloy. Good agreement is obtained

between the HP calculation of the total energy of the order-disorder transformation and specific-heat measurements of this energy. A consequence of present screening calculations^{1,2} is the ordering energy is long-range and oscillatory. The magnitudes of even the far-neighbor ordering-energy terms are not negligible while the second-neighbor energy may be as high as 30% of the first-neighbor term. Walker and Keating⁴ recently measured the neutron diffuse scattering of β -CuZn. Although they do not obtain explicit order parameters,

* This work was performed under the auspices of the U. S. Atomic Energy Commission.

¹ A. Paskin, *Bull. Am. Phys. Soc.* **7**, 216 (1962); R. J. Harrison and A. Paskin, *J. Phys. Radium* **23**, 613 (1962).

² B. D. Silverman and P. R. Weiss, *Phys. Rev.* **114**, 989 (1959); W. Kohn and S. H. Vosko, *ibid.* **119**, 912 (1960); R. J. Harrison and A. Paskin, *J. Phys. Soc. Japan* **15**, 1902 (1960).

³ N. F. Mott, *Proc. Phys. Soc. (London)* **49**, 258 (1937).

⁴ C. B. Walker and D. T. Keating, *Phys. Rev.* **130**, 1726 (1963).