

# Kinetics of Vacancy-Interstitial Annihilation. I. Impurity-Interstitial Trapping\*

A. C. DAMASK† AND G. J. DIENES  
*Brookhaven National Laboratory, Upton, New York*

(Received August 21, 1961)

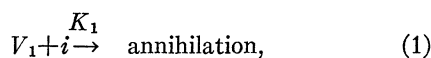
The equations for the kinetics of vacancy-interstitial annihilation with interstitial trapping at impurities have been solved in closed form. Although the transients are given by rather complex combinations of exponentials the later part of the decay is simple quadratic. This quadratic decay is governed by the decomposition of the interstitial-impurity complex. The effective activation energy is the sum of the interstitial migration energy and its binding energy to the impurity.

## I. INTRODUCTION

AS part of the continuing theoretical study<sup>1</sup> of the kinetics of defect annealing in solids, the suggestion of Hasiguti<sup>2</sup> concerning the importance of impurities in the kinetics of interstitial-vacancy annihilation has been examined. The physical model under investigation is the following one. Equal concentrations of vacancies and interstitials have been produced by irradiation. The sample contains a certain concentration of impurities which can trap interstitials with a significant binding energy to form a nonmobile complex. The defects and the impurities are assumed to be randomly distributed in the solid. The present study is restricted to the condition that vacancies and interstitials can decay only by vacancy-interstitial annihilation. The interstitials are assumed to be much more mobile than the vacancies.

## II. GENERAL FORMULATION

Let the following notation be used:  $V_1$ =mono-vacancy concentration (atomic fraction),  $i$ =free interstitial atom concentration (atomic fraction),  $I$ =free impurity atom concentration (atomic fraction),  $I_0$ =total impurity atom concentration (atomic fraction),  $C$ =interstitial-impurity complex concentration (atomic fraction) (one interstitial trapped for one complex formed), and  $N$ =total defect concentration (atomic fraction). The above physical picture is described by the simple kinetic scheme:



This kinetic scheme is described by the following differential equations:

$$dV_1/dt = -K_1 V_1 i, \quad (3)$$

$$di/dt = -K_1 V_1 i - K_2 i(I_0 - C) + K_3 C, \quad (4)$$

$$dC/dt = K_2 i(I_0 - C) - K_3 C, \quad (5)$$

$$N = V_1 + i + C = 2V_1, \quad (6)$$

$$dN/dt = -2K_1 V_1 i, \quad (7)$$

and

$$V_1 = i + C; \quad V_1^0 = i^0, \quad (8)$$

since the number of vacancies is always equal to the total number of interstitials in the sample. Both  $K_1$  and  $K_2$  are determined by the diffusion coefficient for the interstitial atom to a substitutional stationary trap, and therefore,  $K_1 = K_2$ .

With the use of Eq. (8) and with  $K_1 = K_2$  the differential equations may be written in a more convenient form,

$$dV_1/dt = -K_1 V_1 i, \quad (9)$$

$$di/dt = -K_1 i(i + I_0) + K_3 C, \quad (10)$$

$$dC/dt = K_1 i(I_0 - C) - K_3 C. \quad (11)$$

These equations may be solved by the substitution<sup>3</sup>  $u = C/i$  which gives an immediately integrable expression for  $u$ . The result is

$$u = \frac{(K_1/K_3)I_0(C_0 + i_0)e^{\alpha t} + [C_0 - (K_1/K_3)I_0 i_0]}{(C_0 + i_0)e^{\alpha t} - [C_0 - (K_1/K_3)I_0 i_0]}, \quad (12)$$

with  $\alpha = K_1 I_0 + K_3$ . Substitution of  $C/u$  for  $i$  in (9) gives

$$u dV_1/dt = -K_1 V_1 C, \quad (9a)$$

and addition of (9a) to (9) eliminates  $C$  via Eq. (8) to give

$$dV_1/K_1 V_1^2 = -dt/[1 + u(t)], \quad (13)$$

where  $u(t)$  is given by Eq. (12). Upon integration and some algebraic manipulation the final results for  $V_1$ ,  $i$ , and  $C$  are

\* Work performed under the auspices of the U. S. Atomic Energy Commission.

† Guest scientist from Pitman-Dunn Laboratories, Frankford Arsenal, Philadelphia, Pennsylvania.

<sup>1</sup> A. C. Damask and G. J. Dienes, Phys. Rev. **120**, 99 (1960); Discussions Faraday Soc. (to be published).

<sup>2</sup> R. R. Hasiguti, J. Phys. Soc. Japan **15**, 1807 (1960).

<sup>3</sup> We are indebted to S. Narisi of Frankford Arsenal for obtaining this solution and for extensive help on the calculations.

$$V_1 = \frac{[(K_1/K_3)I_0 + 1](C_0 + i_0)\alpha}{K_1\alpha(C_0 + i_0)t + K_1[C_0 - (K_1/K_3)I_0i_0](e^{-\alpha t} - 1) + [(K_1/K_3)I_0 + 1]\alpha}, \quad (14)$$

$$i = \frac{\alpha(C_0 + i_0) - \alpha[C_0 - (K_1/K_3)I_0i_0]e^{-\alpha t}}{K_1\alpha(C_0 + i_0)t + K_1[C_0 - (K_1/K_3)I_0i_0](e^{-\alpha t} - 1) + [(K_1/K_3)I_0 + 1]\alpha}, \quad (15)$$

$$C = \frac{\alpha(C_0 + i_0)(K_1/K_3)I_0 + \alpha[C_0 - (K_1/K_3)I_0i_0]e^{-\alpha t}}{K_1\alpha(C_0 + i_0)t + K_1[C_0 - (K_1/K_3)I_0i_0](e^{-\alpha t} - 1) + [(K_1/K_3)I_0 + 1]\alpha}. \quad (16)$$

### III. DISCUSSION

#### 1. Low-Temperature Approximation

From the kinetic scheme, Eqs. (1)–(2), one expects the following behavior. At low temperature, where the dissociation of the complex is negligible, the concentration of free interstitials approaches zero since a certain fraction of them will be trapped while the rest will be annihilated by recombination with vacancies. At the same time the vacancies and complexes will approach a limiting concentration. This situation corresponds to  $K_3 = 0$  in Eqs. (14)–(16), which, with initial complex concentration zero,  $C_0 = 0$ , reduce to

$$V_1 = \frac{I_0i_0}{(I_0 + i_0) - i_0e^{-K_1I_0t}}, \quad V_1 \rightarrow \frac{I_0i_0}{I_0 + i_0} \text{ as } t \rightarrow \infty; \quad (17)$$

$$i = \frac{I_0i_0}{(I_0 + i_0)e^{K_1I_0t} - i_0}, \quad i \rightarrow 0 \text{ as } t \rightarrow \infty; \quad (18)$$

$$C = \frac{I_0i_0(1 - e^{-K_1I_0t})}{[(I_0 + i_0) - i_0e^{-K_1I_0t}]}, \quad C \rightarrow \frac{I_0i_0}{I_0 + i_0} \text{ as } t \rightarrow \infty. \quad (19)$$

These equations show clearly the approach to saturation by means of exponential functions. It is to be noted, however, that none of the relations represents a simple exponential decay or growth.

#### 2. High-Temperature Approximation

Whenever the temperature is high enough for  $K_3$  to be important the annealing process starts off with annihilation of vacancies and interstitials and the simultaneous formation of complexes with  $C$  going through a maximum. This transient is followed by the decay of the defects which is controlled essentially by the decomposition of the complexes. At times long enough for the transients to be negligible a simple kinetic law is obtained. As the exponentials approach zero, Eqs. (14)–(16) become the integrated expressions for simple quadratic decay (see Appendix):

$$\frac{1}{V_1} = \left( \frac{K_3K_1}{K_1I_0 + K_3} \right) t + \left[ \frac{K_1^2I_0}{(K_1I_0 + K_3)^2} + \frac{1}{i_0} \right], \quad (20)$$

$$\frac{1}{i} = K_1t + \left[ \frac{K_1^2I_0}{K_3(K_1I_0 + K_3)} + \frac{K_1I_0 + K_3}{K_3i_0} \right], \quad (21)$$

$$\frac{1}{C} = \left( \frac{K_3}{I_0} \right) t + \left[ \frac{K_1}{K_1I_0 + K_3} + \frac{K_1I_0 + K_3}{K_1I_0i_0} \right]. \quad (22)$$

The total defect concentration,

$$N = i + C + V_1,$$

will not generally decay strictly quadratically. This will only happen if  $i$  is negligible in comparison with  $V_1$  and  $C$  and if  $K_3 < K_1I_0$ . Under these circumstances

$$C = V_1 = \frac{1}{(1/I_0 + 1/i_0) + (K_3/I_0)t},$$

and, therefore,

$$1/N = \frac{1}{2}(K_3/I_0)t + \frac{1}{2}(1/I_0 + 1/i_0). \quad (23)$$

However, Eq. (23) is a good approximation in practice even when  $i$  is not negligible.

The asymptotic solutions, Eqs. (20)–(22), can also be obtained by a steady-state approximation on  $i$  as shown in the Appendix. This procedure leads to a quadratic differential equation on  $C$  and the same solution as that given by Eq. (22).

Some decay curves were calculated with Eqs. (14)–(16). The constants  $K_1$  and  $K_3$  are given by

$$K_1 = 30\nu e^{-E_i/KT}, \\ K_3 = 5\nu e^{-(E_i+B)/KT},$$

where  $\nu = 10^{13}$ ,  $E_i$  = activation energy for interstitial migration, and  $B$  = binding energy of interstitial to impurity. The combinatory numbers were evaluated on the assumption that the interstitial is in the "split" configuration.<sup>4</sup>

Two typical examples are shown in Figs. 1 and 2 with the various parameters as indicated. The transients are clearly shown, and for decay past the arrows the quadratic approximations of Eqs. (20)–(22) are valid. The total defect concentration,  $N$  (not shown on the graph), also decays very closely as a quadratic

<sup>4</sup> H. B. Huntington, Phys. Rev. **91**, 1092 (1953); J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, *ibid.* **120**, 1229 (1960).

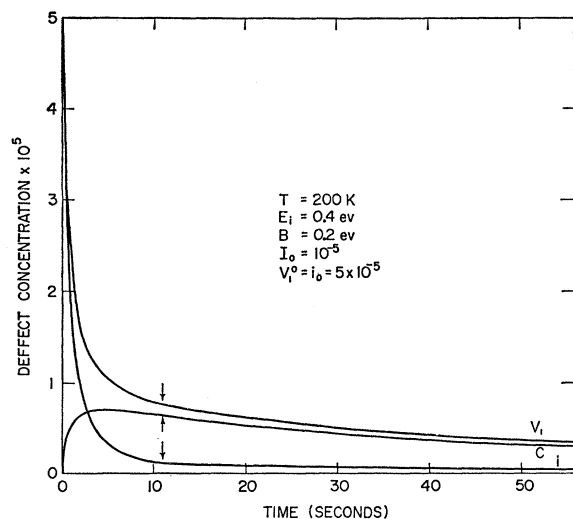


FIG. 1. Plot of Eqs. (14)–(16) for selected parameters. Arrows indicate beginning of quadratic decay.

beyond the arrows. An important result of this calculation is that quadratic kinetics is obeyed at long times even though the reaction is controlled by the decomposition of complexes rather than direct vacancy-interstitial annihilation.

A few isochronals were also calculated with  $E_i = 0.2$  eV and  $B = 0.2$  eV in  $10^\circ\text{C}$ - and 10-sec steps. These values for the energies were chosen to illustrate the clear separation of the low- and high-temperature processes when  $E_i$  and  $(E_i + B)$  differ appreciably. Some representative curves are shown in Fig. 3. Comparison of curves 3(a) with 3(b) shows the influence of

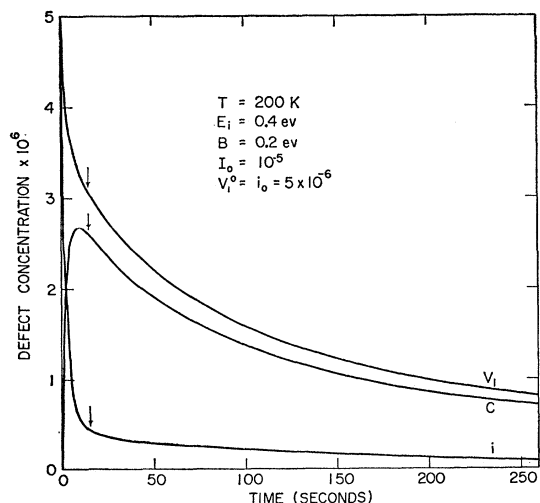


FIG. 2. Plot of Eqs. (14)–(16) for selected parameters. Arrows indicate beginning of quadratic decay.

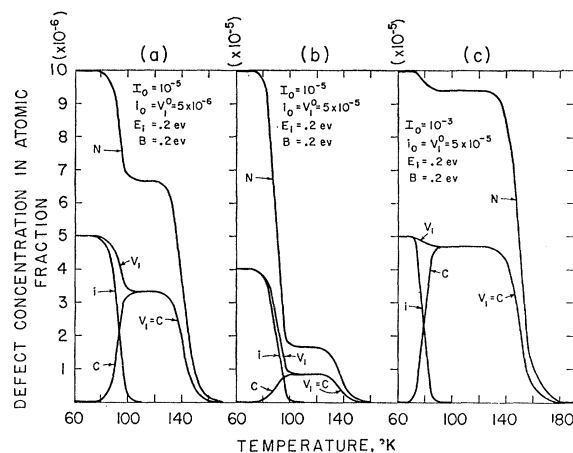


FIG. 3. Ten second-ten degree isochronal curves calculated with Eqs. (14)–(16). (a)–(b): Comparison at two different initial concentrations. (b)–(c): Comparison at two different impurity levels.

initial concentration in the decay curves for the same impurity concentration. Figures 3(b) and (c) show the comparison of decay for the same initial concentration of defects at two different levels of impurity content.

## APPENDIX

If, after the transient, steady-state approximation is assumed for  $i$  in Eq. (10) of the text, then

$$K_3 C = K_1 i (i + I_0),$$

which for  $i \ll I_0$  gives

$$i = (K_3/K_1)(C/I_0). \quad (\text{A1})$$

This relation between  $i$  and  $C$  permits one to integrate Eq. (7) of the text in the following manner:

$$\frac{dN}{dt} = \frac{2dC}{dt} + \frac{2di}{dt} = -2K_1 i (i + C). \quad (\text{A2})$$

Substitution for  $i$  and  $di/dt$  from Eq. (A1) gives

$$\frac{dC}{dt} \left( 1 + \frac{K_3}{K_1 I_0} \right) = - \left( 1 + \frac{K_3}{K_1 I_0} \right) \frac{K_3}{I_0} C^2, \quad (\text{A3})$$

which immediately integrates to

$$1/C = - (K_3/I_0)t + 1/C_0, \quad (\text{A4})$$

which is the same as Eq. (22) of the text.

It is to be noted that if  $di/dt$  is taken to be zero in the differential Eq. (A2), one still obtains a quadratic form but with the incorrect coefficient.