

Kinetics of Vacancy-Interstitial Annihilation. III. Interstitial Migration to Sinks*

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The kinetics of vacancy-interstitial annihilation when interstitials are permitted to anneal at sinks has been studied both by analytic and computer techniques. During the annealing the interstitial concentration decays to zero but the vacancy concentration approaches a terminal value governed by an analytic relation between the concentration of interstitials and vacancies, valid at all times, and independent of the annealing temperature but a function of the sink and initial defect concentration. The growth of defect concentration during irradiation at a temperature where the interstitials are mobile has also been studied. The interstitial concentration goes through a maximum as a function of irradiation time. Past this maximum a steady-state approximation is valid and the subsequent growth of the vacancy concentration can be described by a simple relation. The vacancy growth in steady state is independent of the temperature and is only a function of the integrated exposure. The rate of vacancy accumulation during continuous irradiation is compared to that arising from intermittent irradiations (low temperature) and annealings.

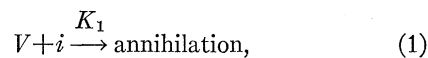
I. INTRODUCTION

THE kinetics of vacancy-interstitial annihilation with two characteristic side reactions, impurity-interstitial trapping and di-interstitial formation, has been presented in previous papers.¹ The above two side reactions are dominant whenever the concentration of the radiation-induced defects is high relative to the sink concentration, i.e., disappearance of interstitials at dislocations is small compared to the other reactions. For simplicity of the kinetic scheme, the escape of interstitials to dislocations was therefore neglected. At low defect concentrations in an ideally pure metal, impurity trapping does not occur and di-interstitial formation can be neglected for low binding energies. It is therefore of interest to examine the condition of vacancy-interstitial annihilation when some interstitials are permitted to escape.

The simultaneous reactions of vacancy-interstitial annihilation and interstitial migration to sinks will be examined for two different conditions. In the first, the irradiation is assumed to occur at a sufficiently low temperature to prevent the motion of the defects. After a given defect concentration has been produced, the sample is raised to a temperature high enough to allow the interstitials (assumed to be the faster moving defect), but not the vacancies, to migrate. The kinetics of interstitial-vacancy annihilation with interstitial migration is then calculated. After the interstitials have disappeared, the sample is assumed to be irradiated again at low temperature and, since there are some residual vacancies present from the previous irradiations, the kinetics of the subsequent annealing is different. Each irradiation followed by annealing will be called a "cycle," and the accumulation of vacancies will be examined for several cycles, a case somewhat analogous to the accumulation of damage in a material

subjected to on and off reactor operation. This over-all process will be referred to as "low-temperature irradiation." The second situation of interest may be called "ambient temperature irradiation." In the analysis of this condition it is assumed that the irradiation is performed at a temperature at which the interstitials, but not the vacancies, can migrate as soon as they are created. This dynamic condition is similar to a series of infinitely short cycles of the first type of experiment. The process of vacancy accumulation will be compared for the two types of irradiations as a function of the integrated exposure.

The kinetic scheme for both conditions is



where V is the vacancy concentration in atomic fraction and i is the interstitial concentration in atomic fraction. (Since the rate of formation of di-interstitials is proportional¹ to i^2 , a quantity comparable in magnitude to the product of the vacancy and interstitial concentrations, Vi , its omission from this analysis, and therefore the above reaction, may appear arbitrary. This approximation is discussed in Appendix I).

Corbett, Smith and Walker² have treated some aspects of this problem and have obtained some computer solutions for V as a function of t when annihilation, clustering, and trapping are included in the kinetic equations. They had derived one of the approximations also given in one of our previous papers,¹ as well as the final state of the system after a second low-temperature irradiation (one of the cycles discussed above). In the present paper a detailed analytic discussion is given of the reactions represented by Eqs. (1) and (2) as well as of the generalization of radiation cycling.

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¹ A. C. Damask and G. J. Dienes, *Phys. Rev.* **125**, 444 (1962); G. J. Dienes and A. C. Damask, *Phys. Rev.* **125**, 447 (1962).

² J. W. Corbett, R. B. Smith and R. M. Walker, *Phys. Rev.* **114**, 1460 (1959).

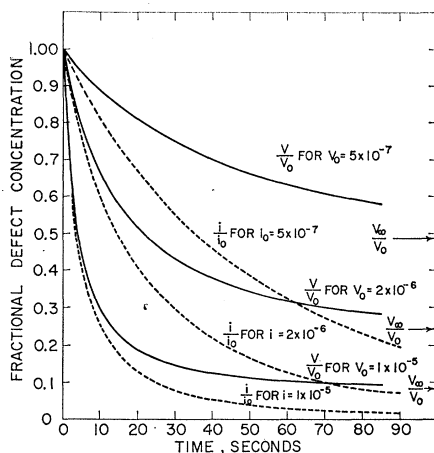


FIG. 1. The decay of vacancies and interstitials for various initial concentrations of defects with equal initial concentrations of vacancies and interstitials. $E_i = 0.1$ eV, $T = 50^\circ\text{K}$. The final vacancy concentration, V_∞/V_0 , is also indicated.

II. LOW-TEMPERATURE IRRADIATION

For the condition of low-temperature irradiation, in which a given defect concentration is present and the sample is then warmed to a temperature at which the interstitials are free to migrate, the differential equations corresponding to the above reactions are

$$dV/dt = -K_1 Vi, \quad (3)$$

$$di/dt = -K_1 Vi - K_2 i. \quad (4)$$

By division of Eq. (4) by Eq. (3) one obtains

$$di/dV = 1 + K_2/(K_1 V), \quad (5)$$

which is integrable and gives

$$i = (i_0 - V_0) + V + (K_2/K_1) \ln(V/V_0). \quad (6)$$

Substitution of i of Eq. (6) into Eq. (3) gives

$$dV/dt = -K_1 V[(i_0 - V_0) + V + (K_2/K_1) \ln(V/V_0)]. \quad (7)$$

This equation is not integrable in terms of elementary functions but is easily solved graphically for V as a function of t .³ Some typical examples of V and i as a function of time are given in Fig. 1, where V is obtained by graphical integration and i is calculated from the equations

$$K_1 = 30\nu e^{-E_i/RT}, \quad (8)$$

$$K_2 = \alpha\nu\lambda^2 e^{-E_i/RT}, \quad (9)$$

where E_i is the migration energy of the interstitial, ν is the vibrational frequency, λ is the jump distance, and α is the effective sink concentration.⁴ These calculations were done at 50°K , and the following values were assigned to the various constants: $E_i = 0.1$ eV, $\nu = 10^{13}$

sec^{-1} , $\lambda^2 = 10^{-15}$ cm^2 , and $\alpha = 10^{10}$ cm^{-2} . In K_1 the 30 is the appropriate combinatory number and was taken from reference 2.

Figure 1 shows the decay of V and i for three different irradiations and, therefore, three different initial concentrations. It has been assumed that the irradiation occurred at a sufficiently low temperature for all the defects to be completely frozen in and that when the sample is warmed to 50°K the interstitials become mobile but the vacancies do not. The following features of these curves are to be noted: (a) i decays much faster than V and approaches zero as t approaches infinity, while V approaches a constant value, V_∞ . (b) The decay of i and V as a function of t obeys no simple law.

It can be seen from Eq. (7) that the temperature dependence of the rate of annealing is controlled by K_1 , and hence by the migration energy of the interstitial, because the ratio K_2/K_1 is independent of the temperature [see Eqs. (8) and (9)]. Thus the curves of Fig. 1 can be calculated for any other temperature via Eqs. (8) and (9). It should be noted that the ratio K_2/K_1 controls the departure from simple bimolecular recombination of vacancies and interstitials. This departure increases with increasing sink concentration since K_2/K_1 is directly proportional to α .

The terminal value, V_∞ , of any given anneal is given by Eq. (6) by setting i equal to zero. Therefore V_∞ is independent of the temperature but does depend on the initial concentrations and on the sink concentration via the ratio K_2/K_1 . The number of interstitials that have been removed from the system at sinks is, of course, equal to V_∞ .

In practice a solid is often irradiated and annealed several times. Experiments of this type carried out under carefully controlled conditions have been done on graphite and have led to valuable information on defect production and annealing processes.⁵ The kinetic scheme under consideration here is simple enough to investigate periodic irradiation and annealing quantitatively. Let the cycle consist of a given irradiation at low temperature (no annealing during irradiation) followed by essentially complete annealing of interstitials at some higher temperature. From Eq. (6) one can calculate V_∞ , i.e., the fraction of vacancies remaining in the sample, after each cycle and add this to the concentration of vacancies introduced by the next irradiation cycle, to correct the initial condition at the beginning of each periodic anneal. Clearly vacancies will accumulate in the sample since a fraction of the interstitials anneal at sinks instead of undergoing recombination. A series of accumulation curves are shown in Fig. 2 for the first 6 cycles for five different irradiation doses, which correspond to 5 different V_0 (and i_0) values representing the fraction of vacancies introduced in each irradiation interval.

³ The solution quoted in Benson's book [S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill Book Company, Inc., New York, 1960), pp. 31-32] for such a system of equations is incorrect.

⁴ See A. C. Damask and G. J. Dienes, *Phys. Rev.* **120**, 99 (1960), footnote on p. 101, for a discussion of α .

⁵ D. G. Schweitzer (to be published).

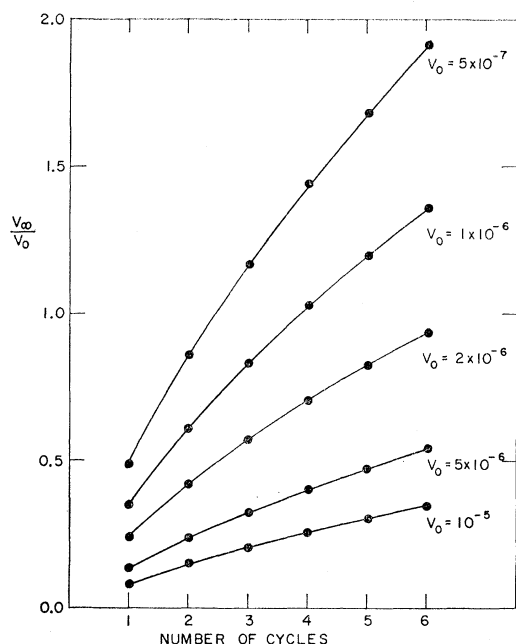


FIG. 2. Accumulation of vacancies as a function of cycles of irradiation for a series of different doses for each cycle. V_0 = atomic fraction of vacancies introduced by radiation at the beginning of each cycle. V_{∞} = atomic fraction of vacancies left in sample after N cycles of irradiation and anneals.

Several points should be noted in connection with Fig. 2. The fraction of vacancies remaining in the sample after a given number of cycles, i.e., the accumulation of vacancies, depends very sensitively on the radiation dosage of each cycle and is large for a short irradiation interval (small V_0), although this fractional increase is not to be confused with total vacancy increase. This is to be expected physically since low concentrations of defects favor interstitial migration to sinks and hence vacancy accumulation. Thus, each successive cycle contributes less residual vacancies to the accumulated total because more of the interstitials combine with the accumulating vacancies. This results in a curvature in the accumulation curves which is clearly seen in Fig. 2 even after a few cycles. In the limit of an infinite number of cycles there are so many vacancies present that all the interstitials recombine and the slopes of the curves of Fig. 2 approach zero. The decrease in the increments of vacancy accumulation is more clearly demonstrated in Fig. 3 where the increments are plotted as a function of the number of cycles. Empirically, these curves are very close to straight lines in a log-log plot, which can, therefore, be used for purposes of extrapolation.

Vacancy accumulation also implies that the rate of annealing in each cycle increases with the number of cycles. This is easily seen from Eq. (7) as a simple concentration effect.

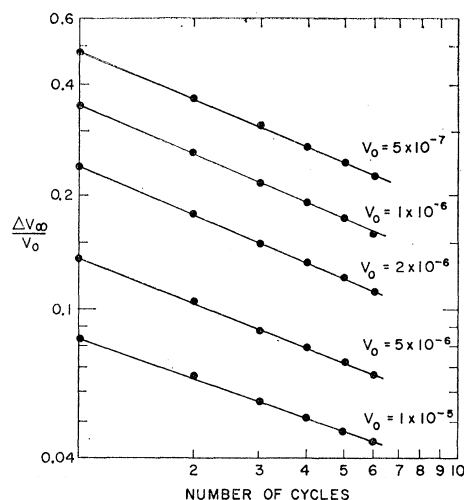


FIG. 3. Fractional increment of vacancy accumulation per irradiation-annealing cycle.

III. AMBIENT TEMPERATURE IRRADIATION

During an ambient temperature irradiation one is interested in the change of concentration of defects during the irradiation at a temperature where the interstitials are mobile. Equations (3) and (4) must be modified by adding a constant, K , which is the constant rate of defect production by the radiation. The corresponding differential equations are

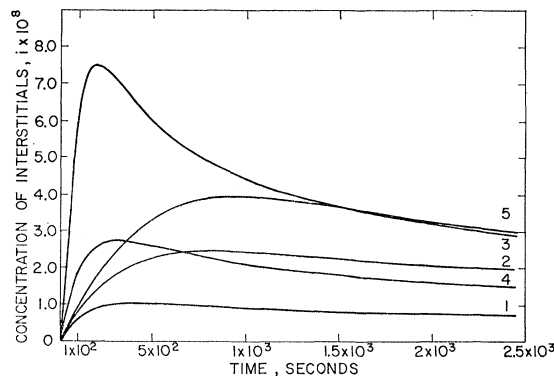
$$dV/dt = K - K_1 Vi, \quad (10)$$

$$di/dt = K - K_1 Vi - K_2 i. \quad (11)$$

These equations cannot be solved in general. Approximations can be made, however, and the validity

FIG. 4. Concentration (atomic fraction) of interstitials vs irradiation time. (Run 6: i concentration is too small to be observable on this scale).

Run No.	Effective sink concentration	Defect production rate (concentration/sec)	Temperature ($^{\circ}$ K)
1	10^{10}	10^{-10}	50
2	10^{10}	10^{-10}	48
3	10^{10}	10^{-9}	50
4	10^{10}	3×10^{-10}	50
5	10^9	10^{-10}	50
6	10^{11}	10^{-10}	50



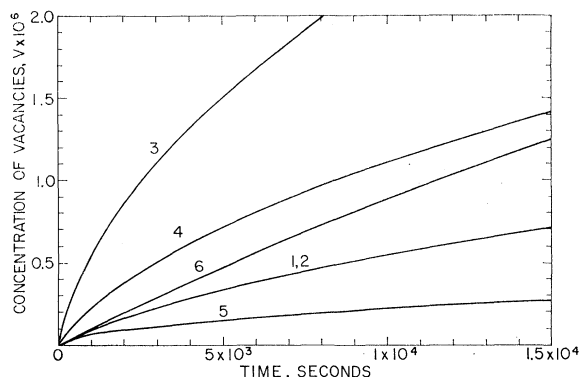


FIG. 5. Concentration (atomic fraction) of vacancies vs irradiation time. Run numbers as in Fig. 4.

investigated by obtaining the complete numerical solution on a computer. An IBM-7090 computer was used and i and V were obtained for a variety of conditions of the parameters of Eqs. (10) and (11). Some typical examples are shown in Figs. 4 and 5. The parameters used in obtaining these curves are given in the captions. It is seen that all of the i curves exhibit a maximum. The magnitude of this maximum and its dependence on the various parameters can be obtained by setting $di/dt=0$ in Eq. (11). This gives

$$i_{\max} = K/(K_2 + K_1 V). \quad (12)$$

Since V is a variable, Eq. (12) can be used only as an approximation in discussing the influence of the various parameters. It is expected that the magnitude of the maximum in i increases with increasing defect production rate and decreases with increasing sink concentration and interstitial mobility. (Interstitial mobility increases with increasing temperature and decreasing migration energy). The computer curves verify these characteristics. No simple theory has been found to determine the time to reach the maximum in i , but the features of this time can be obtained from the computer curves. The time to reach the maximum in i increases with decreasing defect production rate, sink concentration, and mobility.

Equation (12) is also the condition for a steady-state approximation on i . Comparison with the computer solutions showed that Eq. (12) is quite accurately obeyed past the maximum in i . Therefore Eq. (12) can be substituted into Eq. (10) and integrated to give the growth of V with time:

$$V^2 + 2(K_2/K_1)V = 2(K_2/K_1)Kt. \quad (13)$$

This relation was also checked against the computer solutions and found to be accurately obeyed past the value of V that corresponds to the maximum in i . Typical V vs time curves are shown in Fig. 5. The limiting conditions on V can be determined from Eqs. (10) and (11). When no defects are lost to sinks, i.e., $K_1=0$ in Eq. (10), there is an absolute upper bound

in the growth of V given by the value of K . There is also a lower bound on V for any given value of K and at any given temperature. This is obtained by setting $K_2=0$ in Eq. (11) and hence $i=V$. Integration of Eq. (11) with $i=V$ gives the equation of the lower bound as

$$\frac{K + V(KK_1)^{1/2}}{K - V(KK_1)^{1/2}} = \exp[2t(KK_1)^{1/2}]. \quad (14)$$

In Eq. (13) V is not a function of temperature, since K and K_2/K_1 are independent of temperature, but V does depend on the dose and the sink concentration. [Equation (13) is valid only past the maximum in i and the time to reach the maximum, as previously stated, does depend on temperature as well as on K .] It should be noted, however, that in Eq. (13) K only appears as Kt on the right-hand side and therefore all curves for V past i_{\max} can be normalized if plotted against integrated exposure (for neutrons $K=nv$ and $Kt=nv t$). It is of interest to compare the accumulation of vacancies by continuous irradiation at temperature [Eqs. (10) and (11)] with the accumulation arising from periodic irradiation and annealing [Eqs. (1) and (2)]. On the basis of the above discussion this comparison can be done (past the initial transient) independently of K and of temperature if V at any time is plotted against integrated exposure, $nv t$. Figure 6 illustrates this comparison. The curve labeled "continuous growth" is representative of runs 1, 2, 3, and 4 of Fig. 5 since all have the same sink concentration. The curves labeled 1, 2, 3, 4, and 5 are those calculated for Fig. 2 via Eq. (7) with the number of cycles being transformed into $nv t$. Figure 6 shows clearly that the vacancy accumulation is decreased when the mechanism of accumulation involves periodic irradiation and annealing and the annealing consists of the two simple reactions given by Eqs. (1) and (2). The accumulation is smallest for the largest irradiation dosage because the annihilation reaction is favored by a high concentration of defects.

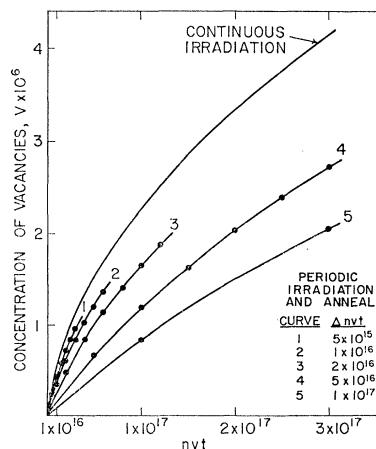


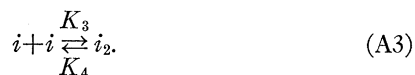
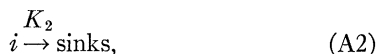
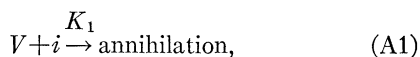
FIG. 6. Comparison of vacancy concentration accumulated by continuous irradiation with vacancy concentration accumulated by periodic low-temperature irradiation and annealing.

ACKNOWLEDGMENT

Appreciation is expressed to Miss E. Wolfson for obtaining the computer solutions.

APPENDIX I

If di-interstitial formation is also to be taken into account, one has the kinetic scheme



The corresponding differential equations are

$$dV/dt = -K_1Vi, \quad (\text{A4})$$

$$di/dt = -K_1Vi - K_2i - K_3i^2 + K_4i_2, \quad (\text{A5})$$

$$di_2/dt = (1/2)K_3i^2 - (1/2)K_4i_2. \quad (\text{A6})$$

These equations reduce to Eqs. (3) and (4) of the text if the last two terms of Eq. (A5) cancel. This, in turn, implies that the di-interstitials are present either in steady state or are maintained in equilibrium with the free interstitials. In either case $di_2/dt = 0$ and Eqs. (3) and (4) of the text result. This approximation is known to be valid, from a previous study,¹ when the temperature is high and/or the binding energy of a di-interstitial is small.

Statistical Theory of Magnetoelectric Effects in Antiferromagnetics*

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It is shown on the basis of a statistical mechanical calculation involving the molecular field approximation and the free energy that the spin-orbit mechanism previously proposed by the author leads not only to the electrically induced but also to the magnetically induced magnetoelectric effect. In addition, this mechanism is found to lead to a magnetoelectric contribution to the electric susceptibility. For a two-sublattice antiferromagnet, the temperature dependence of the magnetoelectric susceptibilities is shown to be quantitatively different from but qualitatively similar to that predicted in the previous work on a phenomenological basis. Although even purely magnetic data indicate that a two-sublattice model is not strictly applicable to Cr_2O_3 , a comparison of the present theory with experiments suggests (with the help of data on the electric field splitting of certain paramagnetic resonance lines in ruby) that the spin-orbit mechanism accounts for a significant part of the magnetoelectric effects observed in Cr_2O_3 . The Appendix contains a revised derivation of some known thermodynamic relations relevant to magnetoelectric effects. It also contains a proposal, based on thermodynamic and symmetry considerations, that "piezomagnetoelectric" and "gyroelectric" effects may exist.

I. INTRODUCTION

SPIN-ORDERED materials may exhibit an induced magnetic polarization which is proportional to an applied electric field and an induced electric polarization which is proportional to an applied magnetic field. These effects will be referred to, throughout the present paper, as the electrically induced magnetoelectric effect $[(\text{ME})_E]$ and the magnetically induced magnetoelectric effect $[(\text{ME})_H]$, respectively. The $(\text{ME})_E$ effect was first observed experimentally by Astrov¹ and the $(\text{ME})_H$ effect by Rado and Folen.² Additional experiments, carried out independently at this Laboratory and in the U.S.S.R., revealed an anisotropy in the temperature de-

pendence of the magnetoelectric susceptibilities,^{3,4} established new evidence for the existence of antiferromagnetic domains,^{2,4} and resulted in the observation of magnetic annealing effects in an antiferromagnetic material.^{2,4} Single crystals of antiferromagnetic Cr_2O_3 were used in all the experiments cited.

Even before these experiments were performed, it had been pointed out by Landau and Lifshitz⁵ on the basis of thermodynamic and symmetry considerations that magnetoelectric $[\text{ME}]$ effects may, in principle, exist in spin-ordered materials. Subsequently, Dzyaloshinskii⁶

³ V. J. Folen, G. T. Rado, and E. W. Stalder, *Phys. Rev. Letters* **6**, 607 (1961).

⁴ D. N. Astrov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **40**, 1035 (1961) [translation: *Soviet Phys.—JETP* **13**, 729 (1961)].

⁵ L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1960), p. 119. (English translation of a 1958 Russian edition.)

⁶ I. E. Dzyaloshinskii, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **37**, 881 (1959) [translation: *Soviet Phys.—JETP* **10**, 628 (1960)].

* The main results of this paper were presented as part of an invited talk at the Baltimore Meeting of the American Physical Society, March 26, 1962.

¹ D. N. Astrov, *J. Exptl. Theoret. Phys. (U.S.S.R.)* **38**, 984 (1960) [translation: *Soviet Phys.—JETP* **11**, 708 (1960)].

² G. T. Rado and V. J. Folen, *Phys. Rev. Letters* **7**, 310 (1961).