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Radiation Enhanced Diffusion in Solids*

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A simple theory of radiation enhanced diffusion has been worked out which describes the dependence of this enhancement on flux and temperature under steady-state conditions. The theoretical study also shows that the measurement of enhanced diffusion as a function of temperature can indicate the mechanism by which defects are removed from the lattice. Alpha-brass was chosen for the experimental work because it is a kinetically simple system, not complicated by nucleation, in which diffusion is easily followed by measuring the electrical resistivity changes associated with changes in short-range order. The enhanced diffusion rate during irradiation in the Brookhaven reactor has been measured in this alloy at several temperatures in the range 0 to 190°C. This enhancement is independent of temperature from 0 to 150°C, in excellent agreement with the theoretical predictions for the case where the radiation induced defects finally disappear at internal surfaces. Some implications of radiation enhanced diffusion and suggestions for further study are also discussed.

I. INTRODUCTION

THERE are three important effects of neutron irradiation on solid-state rate processes in nonfissionable alloys: (1) enhanced diffusion, (2) enhanced nucleation, and (3) breakup of clusters of ordered or precipitated atoms. In most irradiation studies of alloys various combinations of these effects occur together. In the work to be described, enhanced diffusion has been isolated and studied independently of the other two effects. The theoretical part is concerned with a rather general treatment of the influence on diffusion of excess defects arising from a constant rate of generation of such defects. Thus, the theory is applicable to defect production by a constant strain rate as well as by irradiation. The experimental part is concerned with the detailed study of one alloy, alpha brass. The experimental results and the simple theory are found to be in excellent agreement.

It is generally accepted at the present time that diffusion in solids takes place via defects in the crystal, primarily vacancies in metals, and either vacancies or interstitials in ionic salts.[1] Since fast particle irradiation results in the production of such defects a close connection between diffusion and irradiation is to be expected.[2] Similarly, defects are probably generated during plastic flow[3] and, therefore, changes in diffusion may be expected in the presence of an imposed strain rate large enough to cause dislocation motion.

On the basis of a simple physical argument the following effects are to be expected. An excess number of defects can be produced by irradiation or plastic flow. The defects will tend to anneal out at elevated temperatures leading to a steady-state concentration of defects during irradiation at these temperatures. This steady-state concentration of excess defects is the quantity directly related to diffusion effects. In a typical irradiation of nonfissionable materials the generation rate is usually not high enough to lead to observable effects in a typical self-diffusion experiment.[4] However, the excess steady-state vacancy concentration may be very much larger than the concentration normally in equilibrium at temperatures below the normal self-diffusion range. At these temperatures a very strong enhancement of diffusion can occur during irradiation with energetic particles. These diffusion effects are observable by indirect methods, in contrast to the direct tracer techniques used for self-diffusion. For example, they are observable by the increased rate of ordering in an alloy during irradiation.

Adam and Dugdale[5] and Blewitt and Coltman[6] were the first ones to observe ordering in an alloy, in this case Cu_3Au, brought about by neutron bombardment. If a disordered specimen of Cu_3Au is irradiated in the reactor at a somewhat elevated temperature, say 150°C, the resistivity decreases and approaches the equilibrium ordered value after a long irradiation. Slight ordering can be achieved even at 80°C.[7] Thermal ordering in these cases is far too slow to be observable. Similar effects have been achieved with 1 Mev electrons[8] and with gamma rays.[9] X-ray measurements proved that the long-range order has been increased as a result of the irradiation.[10] The interpretation of these experiments is that the diffusion rate has been increased by the production of vacancies and interstitials during the irradiation. Those defects which are not immediately annihilated by recombination migrate through the

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[1] For recent reviews see F. Seitz, *Phase Transformation in Solids* (John Wiley and Sons, Inc., New York, 1951), pp. 77–145; A. D. LeClaire, *Progress in Metal Physics* (Pergamon Press, Ltd., London, 1953), Vol. 4, pp. 265–332.
[2] See, for example, G. J. Dienes and G. H. Vineyard, *Radiation Effects in Solids* (Interscience Publishers, Inc., New York, 1957).
[3] F. Seitz, Phil. Mag. Suppl. 1, 43 (1952).
[4] R. D. Johnson and A. B. Martin, J. Appl. Phys. **23**, 1245 (1952).
[5] J. Adam and R. A. Dugdale, Nature **168**, 581 (1951).
[6] T. H. Blewitt and R. R. Coltman, Acta Met. **2**, 549 (1954).
[7] Glick, Brooks, Witzig, and Johnson, Phys. Rev. **87**, 1074 (1952).
[8] Adam, Green, and Dugdale, Phil. Mag. **43**, 1216 (1952).
[9] R. A. Dugdale, Phil. Mag. **1**, 537 (1956).
[10] R. R. Coltman and T. H. Blewitt, Phys. Rev. **86**, 641(A) (1952).

crystal leaving a wake of partial order until they are annihilated or trapped either at dislocations or at severely damaged regions of the lattice.

Another set of experiments was performed by Rosenblatt, Smoluchowski, and Dienes on α-brass.[11] These workers found that reactor irradiation of α-brass at 50°C resulted in a decrease in electrical resistivity, and they interpreted this change as an increase in the short-range order. Damask[12] investigated these resistivity effects in some detail by studying the annealing kinetics of resistance changes produced in 30% Zn α-brass by quenching, neutron irradiation at 50°C, and cold work. His studies indicate the following: (1) Resistance decreases in α-brass can be induced by proper heat treatment. The rate of change of resistance with annealing time follows the same kinetics as that of stress induced changes in local order. Thus, the resistance changes arise from changes in short-range order. (2) Reactor irradiation of α-brass at 50°C in an equilibrium resistance state produces a decrease in resistance. An anneal of this decrease results in the same kinetic behavior as that of stress induced order and, therefore, neutron irradiation has increased the short-range order. Further experiments indicated that the change in relaxation time upon irradiation can be very large.[13] At 50°C the thermal relaxation time is about 10^{11} sec while the relaxation time at 50°C in a neutron flux ($2\times10^{12}n/cm^2/sec$) or 2 Mev electron flux ($2\times10^{14}e/cm^2/sec$) is about 10^4 sec. The ratio of the thermal to irradiation relaxation time is about 10^7. Electron irradiation has been found to be considerably less efficient than reactor irradiation, presumably because of easy recombination of nearby interstitial-vacancy pairs. (3) The first step of annealing of resistance induced by cold work shows essentially the same kinetic behavior as (1) and (2), and, therefore, this step probably arises from reordering of the cold work induced disorder. This first step is not annealed by neutron irradiation which shows that local heating from neutron irradiation is not an important mechanism in changing the state of local order. The defects themselves are ineffective in this case because they are apparently trapped by dislocations introduced by the cold work.

These two sets of experiments fully support the conclusion that local or microdiffusion can be greatly enhanced by the presence of the extra defects produced by fast particle irradiation.

Considerable enhancement of the rate of self-diffusion has been observed in the presence of creep strain. Early experiments on iron by Buffington and Cohen[14] have shown that the enhancement of the diffusion rate, expressed as D'/D (D'=diffusion coefficient under applied stress, D=normal diffusion coefficient), is approximately linearly related to the applied steady creep rate, $\dot{\epsilon}$. Similar observations have been presented recently by Lee and Maddin[15] on the effect of torsional strains on self-diffusion in silver. More detailed data have also become available on iron.[16] In particular, it has been shown that the enhancement in iron is temperature sensitive and that the apparent activation energy decreases as the strain rate is increased.

The foregoing experimental results have been interpreted qualitatively on the basis of vacancy formation during creep. This interpretation is reasonable in view of Seitz's[3] considerations concerning the generation of vacancies by moving dislocations. Vacancies rather than interstitials are probably produced in most close-packed metals because of the high energy of formation of an interstitial. If, however, the defects are produced essentially geometrically, vacancy-interstitial pairs may well be created.[17] The latter case is, of course, the important one in connection with radiation effects.

The purpose of this paper is to outline a simple theory of radiation enhanced diffusion and to describe detailed experimental studies on the influence of irradiation on the rate of ordering (short-range) of α-brass. Some aspects of the theory have been treated by Lomer[18] and Nabarro.[19] Attention will be focused here on the dependence of diffusion on rate of defect generation and temperature in various cases. It will be shown that the temperature dependence is governed by different combinations of activation energies in various simple cases of defect production and annealing. Thus, α-brass was chosen for the experimental work because it is a kinetically simple system in which diffusion is easily followed by measuring the change in short-range order, which in turn is done by following the associated changes in electrical resistivity.

II. THEORY

During irradiation vacancies and interstitials are created at a constant rate. At temperatures where the vacancies and interstitials are mobile they anneal out by various mechanisms, such as migration to internal or external surfaces, direct annihilation of vacancies and interstitials in pairs, etc. These opposing processes result in a steady-state concentration of defects in excess of the thermodynamic concentration characteristic of the temperature in question. Once the steady-state concentration of defects has been evaluated the corresponding diffusion constants are easily calculated,

[11] Rosenblatt, Smoluchowski, and Dienes, J. Appl. Phys. **26**, 1044 (1955).
[12] A. C. Damask, J. Appl. Phys. **27**, 610 (1956).
[13] A. C. Damask, Phys. and Chem. Solids **4**, 177 (1958).
[14] F. S. Buffington and M. Cohen, Trans. Am. Inst. Mining Met. Engrs. **194**, 859 (1952).
[15] C. H. Lee and R. Maddin, AEC Conference on Solid State Metallurgy, Rensselaer Polytechnic Institute, Troy, New York, June 11–12, 1957 (unpublished).
[16] See Ujiiye, Averbach, and Cohen, reference 15.
[17] For a detailed discussion see A. Seeger, *Handbuch der Physik, VII. I. Kristallphysik I.* (Springer-Verlag, Berlin, 1955).
[18] W. M. Lomer, AERE (Harwell) Report 1540 (1954) (unpublished).
[19] F. R. N. Nabarro, *Deformation of Crystals by the Motion of Single Ions, Strength of Solids* (The Physical Society, London, 1948), pp. 75–90.

since they are proportional to the over-all defect concentration. The theory given below is valid as long as the steady-state concentration assumption is valid, i.e., as long as the buildup time is short compared to the duration of the experiment. At very low temperatures the defects are frozen-in and the simple theory is not valid. Enhanced diffusion is also obtainable in this latter case when the irradiated sample is warmed to the temperature where the defects become mobile. In this case, however, the efficiency is low[13] because the rather high concentration of defects present prior to migration leads to an increased probability of recombination, and hence a reduced mean free path of migration prior to annihilation. Further, the effective diffusion constant in this case is time-dependent because the concentration of defects decreases with increasing annealing time. For these reasons, only the case of excess steady-state concentration of mobile defects is treated in this paper.

Lomer[18] has treated some aspects of this problem and formulated a general expression in which the defects disappeared both by means of direct recombination and migration to surfaces and confirmed the qualitative picture given in the introduction. We found it highly advantageous to treat several annealing mechanisms separately because the flux and temperature dependences turn out to be different in every case. In this way, one can demonstrate enhanced diffusion and also obtain information about the annealing mechanisms involved. The details of the theory are described in this section.

The coefficients of self-diffusion are expressed by the following relations, for the vacancy and interstitialcy mechanisms, respectively,

$$D_v = v\nu_v\lambda^2 \tag{1}$$

$$D_i = i\nu_i\lambda^2, \tag{2}$$

where v = atomic fraction of vacancies, i = atomic fraction of interstitials, λ = jump distance, and ν_v and ν_i are the effective jump frequencies for vacancies and interstitials. In thermal equilibrium v and i are given by

$$v_0 = A_1{}^v \exp(-E_f{}^v/kT); \quad A_1{}^v = \exp(S_f{}^v/k), \tag{3}$$

$$i_0 = A_1{}^i \exp(-E_f{}^i/kT); \quad A_1{}^i = \exp(S_f{}^i/k), \tag{4}$$

where E_f and S_f are the energies and entropies of formation. The jump frequencies, as functions of temperature, are given by

$$\nu_v = A_2{}^v \exp(-E_m{}^v/kT); \quad A_2{}^v = A\nu \exp(S_m{}^v/k), \tag{5}$$

$$\nu_i = A_2{}^i \exp(-E_m{}^i/kT); \quad A_2{}^i = A\nu \exp(S_m{}^i/k), \tag{6}$$

where A is a geometrical constant of the order of unity which for convenience is absorbed into ν_v and ν_i in (1) and (2) (and shall be assumed equal to 1 in the calculations), ν = effective vibrational frequency of an atom, and E_m and S_m are the respective activation energies and entropies for motion.

TABLE I. Assumed constants for numerical calculations.

Vacancies	Interstitials
$\lambda^2 = 10^{-15}$ cm^2	$\lambda^2 = 10^{-15}$ cm^2
$\nu = 10^{13}$ sec^{-1}	$\nu = 10^{13}$ sec^{-1}
$A_1{}^v = 1.0$	$A_1{}^i = 10^{-1}$
$A_2{}^v = 10^{15}$ sec^{-1}	$A_2{}^i = 10^{13}$ sec^{-1}
$E_f{}^v = 1.2$ ev $= 27\,600$ cal	$E_f{}^i = 4.0$ ev $= 92\,000$ cal
$E_m{}^v = 0.8$ ev $= 18\,400$ cal	$E_m{}^i = 0.2$ ev $= 4600$ cal
$\alpha_v = 10^5$ cm^{-2}	$\alpha_i = 10^5$ cm^{-2}
$K = 10^{-10}$ sec^{-1}	$K = 10^{-10}$ sec^{-1}

All numerical computations were carried out for a representative metal (such as copper) characterized by the constants listed in Table I. Since $E_f{}^i$ is large and, therefore, the concentration of interstitials in thermal equilibrium is very small, D_i was taken as zero in all calculations. In Table I, K is the rate of production of defects and was chosen by the following argument. A typical reactor exposure of 10^{20} n/cm^2 produces, very approximately, 1.0% of displaced atoms.[2] A neutron flux of 10^{12} nv gives, therefore, 10^{-10} vacancies and interstitials per second. Here, K for defect generation by plastic deformation may be considerably larger than for a typical reactor irradiation. Seitz[3] suggests that 10^{-4} atomic fraction of vacancies may be produced by unit strain ($\epsilon = 1$). Thus, at a strain rate of $\dot{\epsilon} = 1$ hr^{-1},[15] K may easily be as high as 10^{-7} sec^{-1}. Thus, effects on self-diffusion, which are small in a typical irradiation, become quite large for diffusion in the presence of creep, in agreement with experimental observations.[14–16] The significance of α is discussed in the next section.

1. Linear Annealing of Defects

It is assumed in this case that the defects disappear by migration to fixed sinks, such as dislocations, internal surfaces, or external surfaces. If v and i are the atomic fraction of vacancies and interstitials in excess of thermodynamic concentrations, then in steady state the concentrations are given by

$$dv/dt = K - K_v v = 0 \tag{7}$$

$$di/dt = K - K_i i = 0, \tag{8}$$

where K is the constant rate of defect production by radiation and is taken to be temperature independent, and K_v and K_i are the characteristic proportionality constants for the rate of removal of the defects. The general results to be given are applicable to defect generation by plastic flow provided this rate of generation can be taken as a constant independent of the temperature. Steady-state approximation is valid as long as the period of defect buildup is short compared to the duration of experiment. The buildup time will be estimated later. At low temperatures the defects are frozen in and this treatment is not valid.

From (7) and (8) one obtains, under steady-state

conditions,

$$v=K/K_v, \tag{9}$$

$$i=K/K_i; \tag{10}$$

K_v and K_i are proportional to the corresponding diffusion constants for vacancies and interstitials, namely,

$$K_v=\alpha_v\nu_v\lambda^2, \tag{11}$$

$$K_i=\alpha_i\nu_i\lambda^2. \tag{12}$$

The proportionality constants can be estimated if it is assumed that vacancies and interstitials are eliminated at dislocations.[2] The result is

$$\alpha_v=\alpha_i=\frac{2\pi N_0}{\ln(r_1/r_0)}, \tag{13}$$

where N_0=number of dislocation lines/cm^2,

$$\pi r_1^2=1/N_0,$$

and r_0=effective radius of cylindrical line of dislocations. There is wide latitude in estimating α. For a well-annealed specimen one may take

$$\alpha_v\cong\alpha_i\cong 10^5, \tag{14}$$

while the present experiments indicate $\alpha_v\cong 10^{10}$ for the samples measured.

Let D' be now the diffusion coefficient under steady-state defect generation. For vacancies one finds

$$D'_v=(v+v_0)\lambda^2\nu_v$$

$$=\frac{K}{\alpha_v\nu_v\lambda^2}\lambda^2\nu_v+v_0\lambda^2\nu_v$$

or

$$D'_v=(K/\alpha_v)+D_v. \tag{15}$$

Similarly, for an interstitial,

$$D'_i=(K/\alpha_i)+D_i. \tag{16}$$

Thus, $D'-D$ is independent of temperature. This is a natural measure of the enhancement of self-diffusion. K is proportional to the flux if vacancies are produced by radiation and to the rate of plastic strain if produced by plastic flow.

The defect concentration is built up according to the time dependent solutions of Eqs. (7) and (8). The results are

$$v=(K/K_v)(1-e^{-t/\tau_v}), \tag{17}$$

where t is measured from the start of irradiation and the buildup time, τ_v, is given by

$$\tau_v=\frac{1}{\alpha_v\nu_v\lambda^2}=\frac{1}{\alpha_v\lambda^2 A_2{}^v}\exp(E_m{}^v/kT). \tag{18}$$

Similarly, for interstitials, the buildup time is given by

$$\tau_i=\frac{1}{\alpha_i\nu_i\lambda^2}=\frac{1}{\alpha_i\lambda^2 A_2{}^i}\exp(E_m{}^i/kT). \tag{19}$$

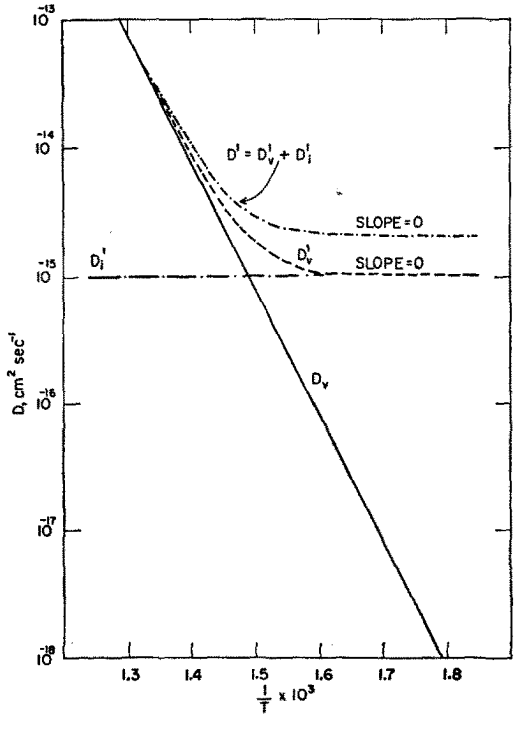

FIG. 1. Enhancement of diffusion by constant generation of defects and their linear annealing by migration to fixed sinks.

The results of some numerical calculations based on Eqs. (15) and (16) are shown in Fig. 1, where the diffusion coefficients enhanced by radiation, D', are compared to the normal thermal diffusion coefficient D_v. If interstitials formed by the radiation take part in the diffusion process then their contribution is the same as that of vacancies. In this case $D'=D_v'+D_i'$ (D_i is taken as zero since thermal interstitial production requires large energies) as shown by the upper curve of Fig. 1. It is clear that enormous enhancement can occur at low temperatures, while the radiation effects are negligible at elevated temperatures. The most important result is that, at temperatures where D_v is small, D' becomes independent of the temperature. This feature is clearly displayed by Eqs. (15) and (16).

The buildup times were calculated from Eqs. (18) and (19) over the temperature range covered in Fig. 1 and were found to be quite short (up to about 10^3 sec at the low temperature end and decreasing rapidly as the temperature increases) compared to experimental time scales. Thus, the steady-state assumption is fully adequate over this range of temperatures and diffusion constants.

2. Annealing of Defects by Direct Recombination

The second simple case is characterized by the annealing of defects by the direct recombination of vacancies and interstitials, which are generated in equal numbers by radiation. Assume first that v_0 is small compared to v; the correction for v_0 is discussed later. It is also assumed that the interstitials migrate much faster than the vacancies (the opposite case is easily treated by symmetry). The simplest direct recombination is described, in steady state, by the relations

$$dv/dt = K - \nu_i v i = 0, \tag{20}$$

$$di/dt = K - \nu_i v i = 0, \tag{21}$$

and $v=i$. Thus, in steady state,

$$v = i = \left(\frac{K}{\nu_i}\right)^{\frac{1}{2}}, \tag{22}$$

and

$$D'_v = \frac{K^{\frac{1}{2}}}{(A_2{}^i)^{\frac{1}{2}}} \lambda^2 A_2{}^v \exp[-(E_m{}^v - \tfrac{1}{2}E_m{}^i)/kT] + D_v \tag{23}$$

and

$$D'_i = K^{\frac{1}{2}}(A_2{}^i)^{\frac{1}{2}}\lambda^2 \exp[-\tfrac{1}{2}(E_m{}^i/kT)] + D_i. \tag{24}$$

In these cases $D'-D$ depends exponentially on $1/T$ with characteristic activation energies given by (23) and (24). Also note that D' depends on $(\text{flux})^{\frac{1}{2}}$ in contrast to the linearity in flux of case 1. The results of numerical computations are shown in Figs. 2 and 3.

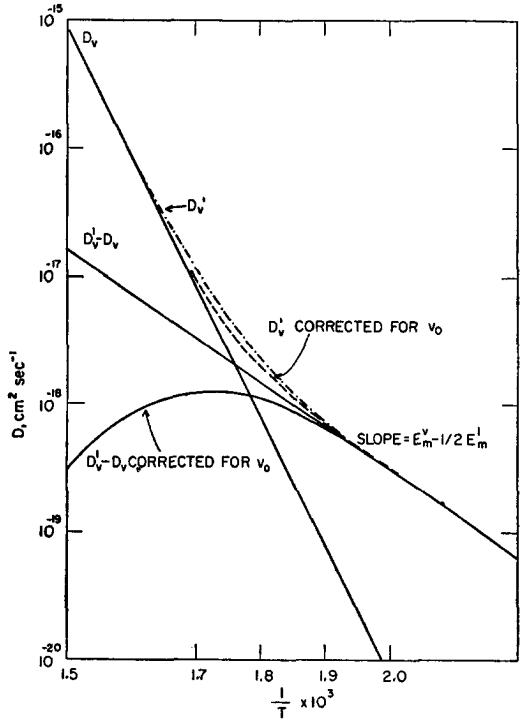

FIG. 2. Enhancement of vacancy diffusion by constant generation of defects and their annealing by direct recombination.

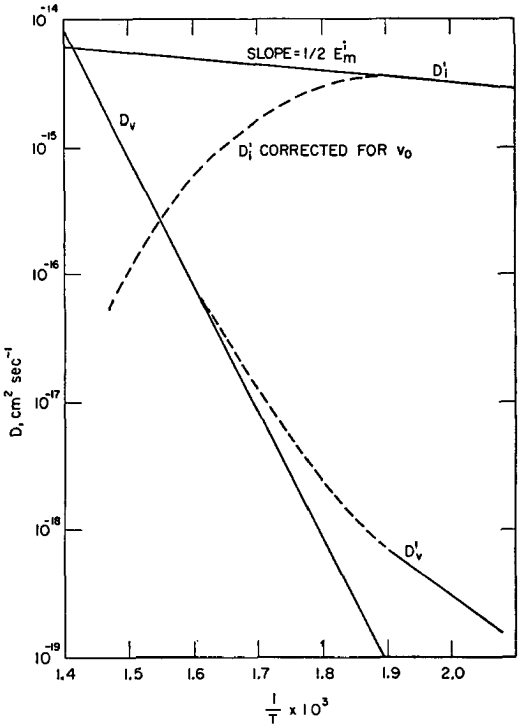

FIG. 3. Enhancement of interstitialcy diffusion by constant generation of defects and their annealing by direct recombination.

The straight line from the top to the bottom of Fig. 2 and labeled D_v is the thermal diffusion rate for the vacancy mechanism. The line labeled $D_v'-D_v$ is the diffusion rate for radiation produced vacancies. However, this curve must be corrected further for the thermal vacancies, v_0.

The influence of v_0 on annealing can be taken into account. If

$$dv/dt = K - \nu_i(v+v_0)i = 0, \tag{25}$$

then

$$v = i = -\frac{v_0}{2} + \frac{1}{2}\left(v_0{}^2 + \frac{4K}{\nu_i}\right)^{\frac{1}{2}}, \tag{26}$$

which can be compared numerically to the simpler case. It is found that this correction is important in the temperature region where enhanced diffusion just becomes significant. The alteration of the curve due to the thermal vacancies is shown by the curves labeled "corrected for v_0" where $D_v'-D_v$ is for the radiation produced vacancies alone and "D_v' corrected for v_0" is the final result when all vacancy effects are considered [see Eq. (26)]. In Fig. 3 D_v and D_v' are the same as in Fig. 2 although shifted to a different scale. The dashed curve labeled "D_i' corrected for v_0" represents the final effect if the material diffuses by an interstitial mechanism only.

The buildup of concentration of defects is given by the time dependent solution of Eq. (20). As steady state is approached the complete solution is well

approximated by

$$v=\left(\frac{K}{\nu_i}\right)^{\frac{1}{2}}\{1-2\exp[-2(K\nu_i)^{\frac{1}{2}}t]\} \tag{27}$$

so that a buildup time τ can be used, given by

$$\tau=\frac{1}{2(K\nu_i)^{\frac{1}{2}}}=\frac{1}{2K^{\frac{1}{2}}(A_2{}^i)^{\frac{1}{2}}}\exp(\tfrac{1}{2}E_m{}^i/kT). \tag{28}$$

The buildup times for this case are even shorter than for case 1, rendering the steady-state region easily accessible to experiment.

3. Linear Anneal Plus Recombination

If both annealing to surfaces and recombination are occurring then, following Lomer's treatment,[18] one has to solve the equations

$$dv/dt=K-K_vv-\nu_i(v+v_0)i=0 \tag{29}$$

$$di/dt=K-K_ii-\nu_i(v+v_0)i=0. \tag{30}$$

After considerable reduction one finds

$$v=-\tfrac{1}{2}(\alpha\lambda^2+v_0)+\tfrac{1}{2}[(\alpha\lambda^2+v_0)^2+4K/\nu_v]^{\frac{1}{2}} \tag{31}$$

$$i=\frac{1}{2\nu_i}\{-(\alpha\lambda^2\nu_v+\nu_vv_0)+\tfrac{1}{2}[(\alpha\lambda^2\nu_v+\nu_vv_0)^2+4K\nu_v]^{\frac{1}{2}}\}. \tag{32}$$

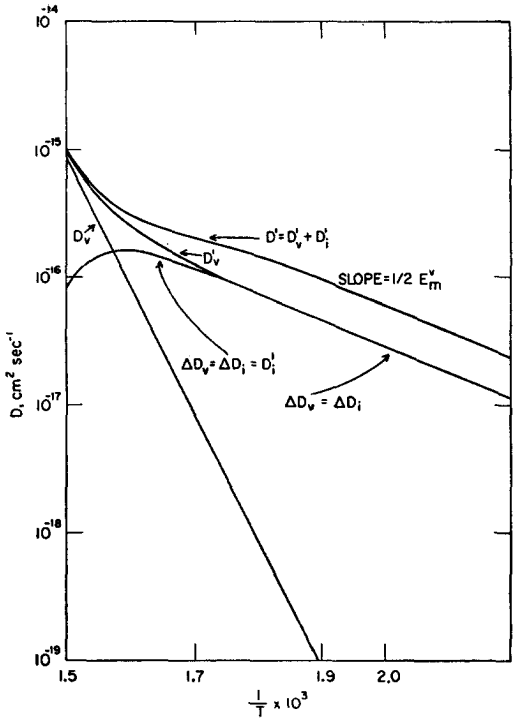

FIG. 4. Enhancement of diffusion by constant generation of defects and their annealing by direct recombination plus simultaneous migration to fixed sinks.

From Eqs. (31) and (32) $i\nu_i=v\nu_v$ and, therefore, $\Delta D_v=\Delta D_i$. At low temperature, where v_0 is small and therefore the enhancement is large, ΔD is dominated by

$$\nu_v(K/\nu_v)^{\frac{1}{2}}=(K\nu_v)^{\frac{1}{2}},$$

which leads to a square root dependence on the flux and an effective activation energy of $\frac{1}{2}E_m{}^v$. The results of the numerical calculations are shown in Fig. 4. The straight line labeled D_v is again the thermal case and D_v' is the final result of radiation enhanced vacancy diffusion using the complete Eqs. (31) and (32).

The buildup time can be estimated by obtaining the time-dependent solution to Eqs. (29) and (30) with the assumptions that i reaches steady state quickly and that v_0 is small. Under these conditions the differential equation is solvable. After considerable algebraic reduction the buildup time, τ, is well approximated by

$$\tau=1/(K\nu_v)^{\frac{1}{2}}.$$

The values of τ are again quite short compared to experimental time scales over the range represented in Fig. 4.

The major conclusion from the theoretical work described in the foregoing is that every annealing mechanism is characterized by a different dependence on flux and temperature in the temperature region where enhanced diffusion dominates. A summary of these results is given in Table II. Thus, it has been demonstrated that large enhancement in diffusion is to be expected in a radiation field in appropriate temperature regions. Further, from the flux and temperature dependence one can draw important inferences about the mechanism of annealing of the radiation induced defects.

Some further remarks should be made at this point. Case 2, pure recombination of vacancies and interstitials, is probably a rather artificial case since the boundary condition $i=v$ was imposed. This boundary condition may not be experimentally accessible since if there is some linear anneal present Case 3 applies. Case 2 was discussed, however, because very direct and interesting results are obtainable if the conditions suitable for this case can be achieved experimentally.

TABLE II. Characteristics of enhanced diffusion for various annealing mechanisms.

Annealing mechanism	Activation energy for enhanced diffusion	Dependence of enhanced diffusion on rate of defect generation (flux)
Linear (direct to surfaces)	0	Linear
Bimolecular recombination of interstitials and vacancies	Vacancies: $E_m{}^v-\frac{1}{2}E_m{}^i$ Interstitials: $\frac{1}{2}E_m{}^i$	Square root
Bimolecular recombination plus linear anneal	$\frac{1}{2}E_m{}^v$	Square root

The numerical computations are based on the assumed parameters of Table I and are illustrative only; i.e., the numbers are not applicable quantitatively to the experimental results described in Sec. III. It turns out that the experiments conform to Case 1 and give, therefore, only one parameter, α. This parameter in our particular experiments is larger than the α assumed in Table I. The only significance of this is to change the level of the curve in Fig. 1 but not its shape. Further, a large α implies a short buildup time [Eq. (18)] rendering the steady-state approximation applicable in our experiments.

III. EXPERIMENTS

Alpha-brass has proved to be a very important alloy for the study of radiation produced defects. The short-range order changes which can be produced by thermal or radiation treatment give rise to a resistivity change. It has been shown theoretically that small changes in short-range order will obey simple exponential kinetics.[20] The resistivity changes which can be produced also obey simple exponential kinetics.‡ It is therefore concluded that small changes in short-range order are linearly related to small changes in resistivity. Furthermore, the relaxation times evaluated from resistivity changes are the same as those obtained by anelastic effects. The kinetics of these processes have been shown to obey an Arrhenius equation over many logarithmic cycles, and this equation yields the same activation energy as diffusion experiments. Thus, the $1/\tau$ values determined in the present work are directly proportional to the diffusion constant, D, at the same temperature, where τ is the relaxation time determined by resistivity measurements. No nucleation is required for a change in short range, nor is there any observable destruction of the order by neutrons during short time irradiations. All defects produced by radiation are mobile down to about -30°C. Because of these virtues and the past irradiation studies that have been made on it, this alloy was chosen to check the theory by experiment.

Brass wires (30% wt Zn) were made, and most of the techniques of annealing and measurement were the same as reported elsewhere.[12,13] Several different techniques were used to obtain the irradiation data and they will be described below. All wires were annealed and then brought to thermal equilibrium at 210°C before measurement. All resistivity data were taken at liquid nitrogen temperature.

Two separate radiation holes in the Brookhaven reactor were used. In one, the ambient temperature is about 50°C, and in the other, whose ambient temperature is about 90°C, there is a furnace in which higher temperatures can be achieved. The flux in the 50° hole

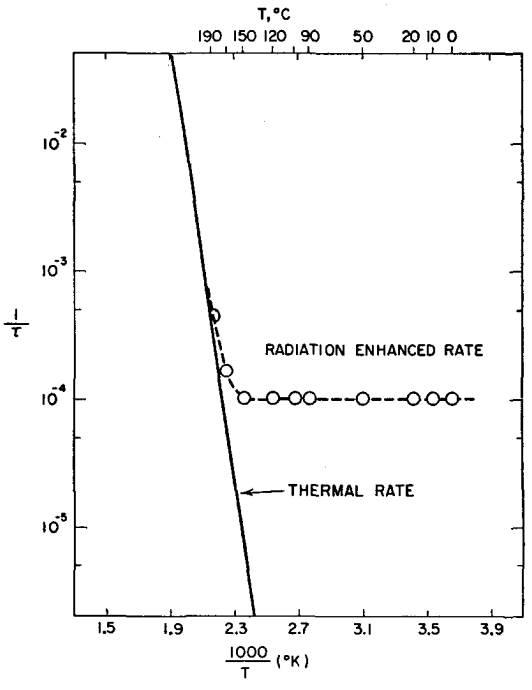

FIG. 5. Rate of ordering $(1/\tau)$ *vs* $1/T$ for alpha brass. Solid line—thermal rate. Dashed line—theoretical radiation enhanced rate. Circles—experimental points.

is about 5×10^{12}, of which about 25% is fast. One wire was irradiated in the 50° hole for various lengths of time. The wire was removed after each irradiation and the electrical resistance was measured at liquid nitrogen temperature. Sufficient points were taken to obtain the curve of the decay of resistivity. An example of this curve is shown in reference 13.§ The relaxation time, τ, for this decay is taken as the time required for the resistivity to fall to $1/e$ of the total amount of resistance decrease. For temperatures below 50°C the irradiation was performed by placing the specimen in a can with an open end loosely packed with aluminum foil. At the closed end of the can there was a brass fitting with an 0.008-in. orifice. An aluminum tube was connected to this orifice and extended out of the reactor to a series of high pressure CO_2 cylinders. A thermocouple alongside the sample was used to monitor the temperature and the CO_2 pressure was varied to maintain the desired temperature. The pressures used were of the order of 500 lb/in.^{2} and the temperatures could be controlled to within ±3°C. One wire was used for the 0° and the 10°C series, with resistance measurements made at liquid nitrogen temperature in between each irradiation. The point at 20°C was obtained by irradiating the previously studied wire for a known time and comparing the amount of resistance

[20] S. Iida, J. Phys. Soc. Japan **10**, 769 (1955).

‡ The kinetics of lattice parameter changes have recently been shown by Feder, Nowick, and Rosenblatt [J. Appl. Phys. **29**, 984 (1958)] to be in agreement with all other kinetic data on this system.

§ The curve shown in reference 13 was taken at a higher flux than in the present experiments giving a relaxation time of 6×10^3 sec. The decay curves used in the present paper approximate closely an exponential decay and under the reactor conditions used in this study all the low temperature curves gave a relaxation time close to 10^4 sec before normalization for flux changes.

decrease with the complete curve that was obtained at 10°C. Figure 5 shows the thermal rate curve as the solid line and the theoretical radiation rate curve as the dashed line. The circles are the experimental points and their estimated accuracy is about the size of the circles.

The higher temperature hole had to be used for the irradiations above 50°C. The neutron flux was lower in this hole so a normalization factor had to be obtained because the accuracy which this experiment required is much greater than the known methods of flux spectrum determination. The wire on which the complete decay curve had been obtained at 50°C was annealed and irradiated for a precise time in the 90°C hole. It was then annealed again and irradiated in the same hole for the same length of time at 100°C. The amount of resistance decrease was identical, which showed that the curve of Fig. 5 was still flat at those temperatures. When this decrease was measured on the complete curve that had been obtained at 50°C the normalization factor was obtained. All data above 50°C are therefore normalized to the flux in the 50°C hole. A number of wires were made up in an identical fashion, i.e., drawn in one piece, annealed together, etc. These wires were equilibrated together and irradiated for different lengths of time at 120°C and a composite resistance decay curve was plotted. The relaxation time was again taken at $1/e$ and normalized to the 50°C hole flux. The same thing was done at 150°C. At 173 and 190°C the relaxation times are relatively short, and the correction factors such as warming time of the sample can become appreciable. Therefore only one irradiation at each temperature was made, of the order of 30 min at 190°C and 45 min at 173°C. The wires were then reannealed at 210°C and the thermal resistance changes at 190 and 173°C were measured as a function of time. The time ratios for in-pile and out-of-pile resistance changes at these two temperatures were obtained. These ratios give the ratios of relaxation times at each temperature. In all of the data above 50°C there is a temperature error of ± 2°C which lies well within the size of the circles. At 190°C the in-pile relaxation time was shorter than the thermal relaxation time so the error cannot lie much below the theoretical curve in this case without falling below the thermal rate curve. This point is therefore indicated by the semicircle. All the experimental data are summarized in Table III and plotted in Fig. 5.

TABLE III. Radiation enhanced diffusion in alpha-brass.

Temp. T°C	1000 T°(K)	Thermal reaction[a] τ(sec)	Reaction in reactor τ'(sec)	$\frac{\tau^b}{\tau'}$
297	1.76	1		~1
262	1.87	10		~1
230	1.99	10^2		~1
202	2.10	10^3		~1
190	2.16	2.5×10^3	2×10^3	1.2
173	2.24	1.2×10^4	5.5×10^3	2.2
150	2.36	1.4×10^5 (extrap.)	10^4	14
120	2.54	3.6×10^6 (extrap.)	10^4	3.6×10^2
100	2.68	6.3×10^7 (extrap.)	10^4	6.3×10^3
90	2.76	3.1×10^8 (extrap.)	10^4	3.1×10^4
50	3.10	2.5×10^{11} (extrap.)	10^4	2.5×10^7
20	3.41	1.3×10^{14} (extrap.)	10^4	1.3×10^{10}
10	3.54	1.6×10^{15} (extrap.)	10^4	1.6×10^{11}
0	3.66	1.6×10^{16} (extrap.)	10^4	1.6×10^{12}

[a] Taken from Fig. 1 of reference 12.
[b] τ = Time to complete 63% of the reaction [$(1-1/e)\times$total exchange].

IV. DISCUSSION

The data of Table III and Fig. 5 are in full agreement with the theoretical predictions for the case of linear anneal of the radiation induced defects. Thus, from the work described in the previous sections, the following conclusions may be drawn.

(1) The theoretically predicted radiation enhanced diffusion has been observed experimentally in alpha-brass. The enhancement ratio, i.e., the ratio of the diffusion constants, becomes very large at the lower temperatures. The enhancement, defined as $D'-D$, which is proportional to the experimental $1/\tau'-1/\tau$, is independent of temperature, as predicted by the theory for linear anneal.

(2) It appears that annealing of defects at dislocations dominates in alpha-brass since the radiation enhanced diffusion becomes temperature independent over the 0 to 150°C range in agreement with the theoretical equations for this case. If the effective activation energy is defined as the slope of the curves in Fig. 5, then during neutron irradiation the activation energy in the above temperature range is zero. Direct recombination of interstitials and vacancies would introduce a temperature dependence well outside the experimental error, even in the interstitialcy case (Table II and Fig. 3). Thus, in this experiment direct recombination can be responsible for only a small fraction of the annealing process.

(3) As long as linear anneal, and hence temperature independent enhancement, dominates one can neither separate vacancy from interstitial motion nor determine any activation energy. If direct recombination can be emphasized experimentally, Case 3 will apply giving a value for $\frac{1}{2}E_m^v$ (see Table II). One way to do this is to use high-energy electrons for the irradiation since in this case one expects that rather closely spaced vacancy-interstitial pairs are formed which will annihilate preferentially by recombination. (It is realized, of course, that the annihilation of very close vacancy-interstitial pairs does not follow bimolecular kinetics. A suitable combination of the basic equations will have to be solved for this case.) One set of experiments at 50°C has shown that, while enhancement is obtained with electron irradiation, the theoretical efficiency relative to neutron irradiation is lower by about a factor of 14.[13] The electron case has not yet been explored over a wide range of irradiation temperatures, a problem of obvious immediate interest.

(4) One may speculate about the applicability of

these results to other alloy systems and different rate processes. The linear annealing case for neutron irradiation is probably rather generally valid except for high atomic weight or fissionable materials where thermal or displacement spikes may play an important role[2] and the mean free path of a knocked-on atom becomes very short. Thus, the neutron radiation enhanced diffusion coefficient is expected to be temperature independent in a wide class of alloys. The radiation enhancement ratio which has been determined for the simple exponential case of alpha-brass can be generalized to predict the behavior of more complex kinetic systems. From the experimentally determined τ values the corresponding average diffusion coefficients may be calculated from[21,22] $D=(a^2/12)1/\tau=10^{-16}1/\tau$, where a is the lattice parameter. From the experimental data one obtains $D'-D\cong D'=K/\alpha\cong 10^{-20}$ cm^2 sec^{-1}. Let the kinetics of a process be describable, for example, by $R=AD^n$ where $R=$ rate and n is an exponent characteristic of the shape of the new phase. Under irradiation, then, $R=A(D')^n$ where D' is the diffusion constant in the radiation field. The present work has shown that, for a fast neutron flux of about 10^{12} nv, D' is about 10^{-20} cm^2 sec^{-1} and is probably proportional to the flux. The results of this work are directly applicable to alloy systems obeying the linear case. More complex relations would apply in the case of direct recombination. For example, if the process is governed by $(D')^n$ the new activation energy becomes $n(E_{\text{effective}})$ where $E_{\text{effective}}$ is given in Table II. Unfortunately the precise kinetic behavior is not known for most phase changes in alloys and, therefore, the foregoing considerations will result in only an order-of-magnitude estimate for the diffusion effect to be expected during irradiation of an alloy. There is little basis at the present time for a quantitative comparison of diffusion in a radiation field with thermal diffusion for other than short-range order kinetics. It was mentioned in the introduction that there are two other effects of neutron irradiation on rate processes in solids: enhancement of nucleation, and breakup of ordered or precipitated clusters by "thermal spikes." Of these three effects, only the diffusion has been treated quantitatively. Until the latter two problems are also isolated and solved independently a complete quantitative prediction of a phase change in an alloy under neutron bombardment cannot be made. The problem of breakup of clusters by "thermal spikes" can be avoided by irradiating with electrons or gamma rays (although gammas have been shown to be rather inefficient for most experiments on enhanced diffusion[9,23]).

The separation of the "thermal spike" effect could be achieved by irradiating an alloy already partially ordered or precipitated and thereby minimizing any nucleation effects. One alloy in which the kinetics are fairly well understood and hence would readily lend itself to this type of experiment is Cu_3Au. In a detailed treatment of the ordering kinetics, Dienes[24] showed that the rate constant could be factored from the kinetic equation, and Vineyard[25] later showed that the vacancy concentration was factorable. Since the radiation enhanced diffusion equations in the present work deal explicitly with the excess number of vacancies, it appears that there is now sufficient theory available for a complete analysis of a simultaneous experiment on thermal and neutron enhanced diffusion in partially ordered Cu_3Au. When the equations for the kinetic behavior of other systems are formulated, the radiation enhanced diffusion effects can be evaluated if the nuclei are already present. Eventually it is hoped that the enhanced nucleation problem will be solved independently. Then the behavior of nonfissionable alloys in a radiation field will be understood quantitatively.

[21] B. G. Childs and A. D. LeClaire, Acta Met. **2**, 718 (1954).
[22] A. D. LeClaire and W. M. Lomer, Acta Met. **2**, 731 (1954).
[23] A. C. Damask (unpublished).
[24] G. J. Dienes, Acta Met. **3**, 549 (1955).
[25] G. H. Vineyard, Phys. Rev. **102**, 981 (1956).