# Energy Dependence of Correlated Recovery in Stage I of Al and Cu†

H. M. SIMPSON AND R. L. CHAPLIN
*Department of Physics, Clemson University, Clemson, South Carolina*
(Received 18 March 1968)

The recovery of the $I_D$ substage of aluminum and copper is examined in terms of a diffusional treatment based on correlated recovery. A theoretical expression is obtained which describes the annealing and includes an easily determined parameter which characterizes the initial distribution function. Theoretical calculations are compared with data obtained from a wide range of atomic recoil energies. Values are also computed for the initial distribution and the average separation of interstitials around their vacancies for various irradiation energies.

## I. INTRODUCTION

EXPERIMENTAL results[1] indicate that most metals have a low-temperature recovery spectrum which includes a number of independent annealing processes. For copper and aluminum, part of this recovery has been defined as the $I_D$ substage.[2] The annealing behavior for the $I_D$ substage is presently explained in terms of the annihilation of interstitials with vacancies by either (1) the correlated recovery of migrating interstitials[2–5] or (2) a superposition of close-pair recovery processes[6,7] which may include some free diffusion.[8–11] The models which include close pairs have been justified by the measured "structure" noted by some investigators.[7–12] In accordance to recent experimental results,[13] we have noted that little, if any, of this occurs in the $I_D$ and $I_E$ recovery region of 0.4 MeV electron irradiated aluminum. Therefore, we are assuming the $I_D$ recovery region can be treated in terms of correlated recovery. Additional justifications for this assumption are given in this paper.

After irradiating copper with 1.4-MeV electrons, Corbett, Smith, and Walker[2] obtained good agreement between theory and experiment for a diffusional analysis of the $I_D$ recovery. Such a diffusional treatment is inherently dependent on the irradiation energy through a distribution function which describes the initial interstitial-vancancy separation. However, no consistent study has been made of the energy dependence of correlated recovery. This paper presents such a study. Sec. II deals with the diffusion problem and presents the solution when a modified exponential distribution function [see Eq. (3)] describes the initial separation between a vacancy and its interstitial. Theory and experiment are compared in Sec. III by examining the energy dependence of $I_D$ recovery for aluminum samples which were irradiated with electrons of 0.19, 0.22, 0.30, and 0.40 MeV. A comparison between theory and experiment is also given for thermal-neutron irradiated copper.[14] Finally, the implications of these results are given in Sec. IV.

## II. TIME-TEMPERATURE DEPENDENCE OF THE ANNEALING

A theoretical model for the $I_D$ recovery should account for the dose independence and for the observed half-width of the $I_D$ substage. Since both of these features prevent a description of the $I_D$ recovery by means of chemical rate theory as a singly activated process, diffusion theory based on correlated recovery is applied.

The time-temperature dependence of the annealing is derived in a manner similar to that of other investigators.[15,16] Specifically, the following assumptions are made:

(1) The interstitial migrates freely in three dimensions.

(2) Interstitial-vacancy annihilation occurs when an interstitial comes within a critical radius $r_0$ of the vacancy.

(3) The initial distribution of interstitials about their vacancies is described by a modified exponential distribution function.

(4) All Frenkel pairs are isolated and uniformly distributed. Thus the equation that describes the annealing is obtained from the expression for a particular pair which is multiplied by the initial number of pairs.

† Work supported by the U. S. Atomic Energy Commission.
[1] R. R. Coltman, C. E. Klabunde, and J. K. Redman, Phys. Rev. **156**, 715 (1967).
[2] J. W. Corbett, R. B. Smith, and R. M. Walker, Phys. Rev. **114**, 1452 (1959); **114**, 1460 (1959).
[3] J. W. Corbett, Phys. Rev. **A137**, 1806 (1965).
[4] W. Frank, A. Seeger, and G. Schottky, Phys. Status Solidi **8**, 345 (1965).
[5] W. Bauer, A. Seeger, and A. Sosin, Phys. Letters **24A**, 195 (1967).
[6] R. von Jan, Phys. Status Solidi **17**, 361 (1966).
[7] T. G. Nilan and A. V. Granato, Phys. Rev. **A137**, 1233 (1965); **A137**, 1250 (1965).
[8] H. I. Dawson, G. W. Iseler, and J. W. Kauffman, in *Lattice Defects and Their Interactions*, edited by R. R. Hasiguti (Gordon and Breach Science Publishers, Inc., New York, 1967).
[9] H. I. Dawson, G. W. Iseler, A. S. Mehner, and J. W. Kauffman, Phys. Letters **18**, 247 (1965).
[10] G. W. Iseler, H. I. Dawson, A. S. Mehner, and J. W. Kauffman, Phys. Letters **17**, 212 (1965).
[11] C. L. Snead, Jr., F. W. Wiffen, and J. W. Kauffman, Phys. Rev. **164**, 900 (1967).
[12] A. Sosin and K. R. Garr, Phys. Rev. **161**, 664 (1967).
[13] H. M. Simpson, T. N. O'Neal, A. B. Pruitt, W. E. Faust, and R. L. Chaplin, Phys. Letters **27A**, 559 (1968).
[14] R. R. Coltman, Jr., C. E. Klabunde, and J. K. Redman, Phys. Rev. **159**, 521 (1967).
[15] R. C. Fletcher and W. L. Brown, Phys. Rev. **92**, 585 (1953).
[16] T. R. Waite, Phys. Rev. **107**, 463, 471 (1957).

Let $P(\mathbf{r},t)dv$ be the probability that an interstitial is in the volume element $dv$ at a distance $\mathbf{r}$ from its vacancy at time $t$. This probability is assumed to obey the diffusion equation

$$\frac{\partial P(\mathbf{r},t)}{\partial t}=D\nabla^2 P(\mathbf{r},t), \tag{1}$$

where $D$ is the diffusion constant, and $\nabla^2$ is the Laplacian. The previous assumptions are equivalent to the following boundary conditions for Eq. (1):

$$P(r\leq r_0, t)=0, \tag{2}$$

and

$$P(\mathbf{r}, t=0)=\frac{N}{r}\exp\left[-\frac{r}{\lambda r_0}\right] \quad \text{for} \quad r>r_0. \tag{3}$$

In Eq. (3), $N$ is a normalization constant and $\lambda$ is a parameter to be determined from experimental data. The probability that a vacancy-interstitial pair is separated a distance $r$ at time $t=0$ is given by

$$\rho(r)dr=(N/r)\exp[-r/\lambda r_0]4\pi r^2 dr, \tag{4}$$

and the normalization constant $N$ is evaluated by requiring

$$\int_{r_0}^{\infty}\rho(r)dr=1. \tag{5}$$

The rate equation is obtained by letting the number of defects which disappear per unit time be equal to the flux of interstitials through a sphere of radius $r_0$ around a particular vacancy. If $n$ is the concentration of interstitials and if at time $t=0$, $n(t=0)=n_0$, then

$$dn/dt=-4\pi r_0^2 n_0 D(\partial P/\partial r)_{r=r_0}. \tag{6}$$

By evaluating $(\partial P/\partial r)_{r=r_0}$ from the solution[17] of Eq. (1), the rate equation becomes

$$dn/dt=-4\pi r_0 n_0 N D\exp(-\beta r_0)\times\left\{\frac{1}{(\pi Dt)^{1/2}}-\beta\exp[\beta(\sqrt{Dt})]^2\operatorname{erfc}[\beta(\sqrt{Dt})]\right\}, \tag{7}$$

where

$$\beta=1/\lambda r_0. \tag{8}$$

Making the substitutions

$$\phi=(n_0-n)/n_0, \tag{9}$$

and

$$Z=(\sqrt{Dt}), \tag{10}$$

Eq. (7) reduces to

$$d\phi/dZ=8\pi r_0 N\exp(-\beta r_0)\times\left[\frac{1}{\sqrt{\pi}}-\beta Z\exp(\beta^2Z^2)\operatorname{erfc}(\beta Z)\right]. \tag{11}$$

A simple parts integration then gives[18]

$$\phi=1/(1+\lambda)\{1-\exp(\beta^2 Dt)\operatorname{erfc}[\beta(\sqrt{Dt})]\}, \tag{12}$$

where the explicit form for the normalization constant $N$ has been used. One notes the following significant features concerning the fractional recovery, $\phi$ as given by Eq. (12):

(1) $\phi$ is a function only of $Dt$.

(2) An experimental evaluation of $\lambda$ is readily accomplished since when $Dt\rightarrow\infty$, then $\phi=1/(1+\lambda)$.

(3) For small $Dt$, $\phi\propto(\sqrt{Dt})$ which is consistent with Waite's description of correlated recovery.

To compare Eq. (12) with isochronal annealing data, we make the constant rate of heating approximation that

$$T=T_0+\alpha t, \tag{13}$$

and we replace $Dt$ by

$$Dt\rightarrow\int_0^t Ddt\rightarrow\frac{D_0}{\alpha}\int_{T_0}^{T}e^{-E_m/kT}dT, \tag{14}$$

where $D_0$ is the constant part of the diffusion constant, $E_m/k$ is the activation energy for free diffusion divided by Boltzmann's constant, and $\alpha$ is the constant heating rate. For small values of $T_0$ and when $kT/Em\ll 1$, Eq. (14) can be closely approximated as

$$Dt\simeq\frac{D_0kT^2}{\alpha E_m}\left(1-\frac{2kT}{E_m}\right)e^{-E_m/kT}. \tag{15}$$

By using the constant rate of heating approximation,[19] a theoretical $\phi$ versus $T$ curve will be shifted by $+\Delta T/2$ in relation to the corresponding isochronal curve. Here $\Delta T$ is the temperature increment between anneals. Another method of comparing Eq. (12) with isochronal data concerns the equivalent time method. One replaces $Dt$ in accordance to

$$Dt\rightarrow D_0\int_0^t e^{-E_m/kT}dt=D_0\Delta t\sum_{i=1}^{n}e^{-E_m/kT_i} \tag{16}$$

via Stieltjes integration, where $\Delta t$ is the constant time spent at each temperature and $n$ refers to the $n$th anneal.

[17] R. Churchill, *Fourier Series and Boundary Value Problems* (McGraw-Hill Book Co., Inc., New York, 1941), p. 122.

[18] J. Crank, *The Mathematics of Diffusion* (Clarendon Press, Oxford, England, 1957), p. 326.

[19] R. Gevers, J. Nihoul, and L. Stals, Phys. Status Solidi **15**, 701 (1966).

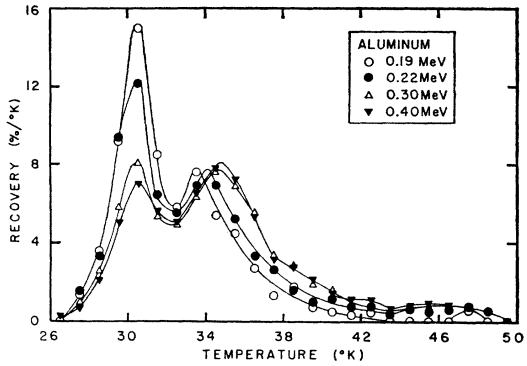


FIG. 1. Isochronal recovery of electron-irradiated aluminum.

The equivalent time[2] $t_n$ is taken as

$$\Delta t \sum_{i=1}^{n} \exp\left[-\frac{E_m}{kT_i}\right]. \tag{17}$$

## III. COMPARISON BETWEEN THEORY AND EXPERIMENT

A previous publication[20] has presented the experimental data for aluminum which was irradiated with electrons whose energy was 0.22, 0.30, and 0.40 MeV. Additional results obtained under similar experimental conditions are presented herein for an 0.19 MeV electron irradiation when the total resistivity change was 0.83 $\times 10^{-10}$ Ω cm. The derivative curves for these data are shown in Fig. 1. For the curves, the $I_C$ recovery is centered at 30°K, the $I_D$ substage has a peak position near 34°K, and $I_E$ is the recovery in the 47°K temperature region. Note how the peak position of the $I_D$ substage shifts to lower temperatures as the irradiation energy is decreased.

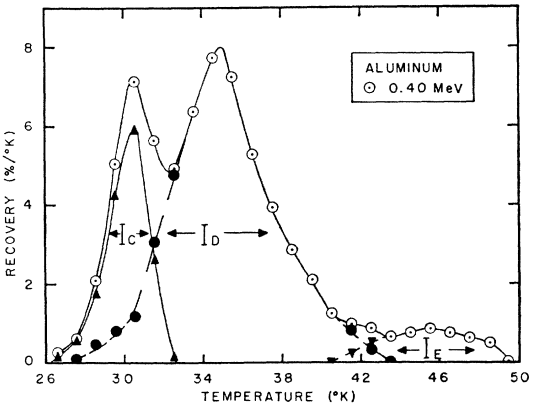


FIG. 2. These curves show how the $I_D$ substage is resolved. The solid triangles represent the calculated values of $I_C$ and the estimated values of $I_E$. These values were then subtracted from the data points to give $I_D$.

[20] R. L. Chaplin and H. M. Simpson. Phys. Rev. **163**, 587 (1967).

TABLE I. Magnitudes of energy-dependent quantities.

| Element | Energy (MeV) | $I_C$ % | $I_D$ % | $I_E$ % | $\langle r \rangle$ (in units of $r_0$) | λ |
|---|---|---|---|---|---|---|
| Aluminum | 0.19 | 29.5 | 39.0 | 0.7 | 1.27 | 0.229 |
| Aluminum | 0.22 | 25.9 | 42.4 | 3.1 | 1.30 | 0.253 |
| Aluminum | 0.30 | 16.6 | 47.5 | 3.9 | 1.42 | 0.335 |
| Aluminum | 0.40 | 15.3 | 47.5 | 4.8 | 1.56 | 0.433 |
| Copper | 1.40 | | 53.4 | | 1.62[a] | 0.470 |
| Copper | $\bar{E}_T$=374 eV[b] | | 43.5 | 8.9 | 2.50 | 1.00 |

[a] Evaluated from the data of Ref. 3.
[b] The average value of the recoil energy, $\bar{E}_T$ was taken from Ref. 1; the average value of $r$ was calculated on the basis of data presented in Fig. 5.

Because of the overlapping of adjoining substages, an approximation must be used to resolve the amount of recovery in individual substages. Thus, the recovery shown in Fig. 1 is subdivided in accordance to (1) $I_C$ obeying first-order kinetics (activation energy of 0.086 eV and frequency factor of $2\times10^{11}$/sec), (2) $I_E$ being symmetrical about its peak position, and (3) the subtraction of $I_C$ and $I_E$ from the experimental curve giving a smooth recovery curve for the $I_D$ substage. A typical result of this procedure is presented in Fig. 2 for the 0.40 MeV data. In accordance to the areas under the various curves on this figure, the fractional amount of recovery for $I_C$, $I_D$, and $I_E$ is, respectively, 15.3%, 47.5%, and 4.8%. This analysis has been repeated for each irradiation energy and the results are presented in Table I.

Experimental values of the $I_D$ substage are plotted in Fig. 3 where the fractional amount of recovery $\phi_D$ excludes close pairs. The solid lines on this figure represent the variations of $\phi_D$ as determined from Eq. (12) when Eq. (17) has been used. Theoretical curves were determined for selected values of λ when $D_0/r_0^2 = 2.5\times10^{12}$/sec and $Em/k = 1320$°K. Assumed values for these quantities which differ by ±10% from the above values will not give curves which can satisfy the experimental data. One notes that the experimental curves show the temperature shift for the $I_D$ recovery and indicate how the fractional amount of recovery

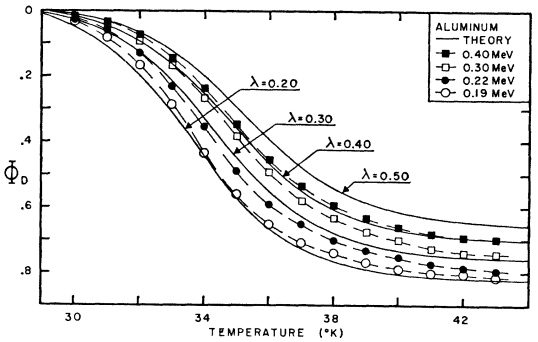


FIG. 3. The fractional recovery $\phi_D$ corresponding to the data from Fig. 1, compared with theory for arbitrary values of λ. The theoretical curves have been shifted $-\frac{1}{2}$°K along the temperature axis in accordance with the constant-rate-of-heating analysis, as explained in the text.

increases as the irradiation energy is decreased. An identical behavior is obtained for the theoretical curves by varying the value of $\lambda$.

The conventional method of plotting $\phi_D$ versus equivalent time is presented in Fig. 4. Experimental values are shown for the 0.40 MeV irradiation, and the solid curve shows the corresponding theoretical behavior. Both curves indicate an identical time-temperature dependence for all of the annealing of the $I_D$ substage.

In order to show that the resultant value of $D_0/r_0^2$ is physically reasonable, it is assumed that the entropy factor is unity and that

$$D_0=\nu a_0^2, \tag{18}$$

where $\nu$ is a frequency factor and $a_0$ is the lattice spacing.[21] By letting

$$r_0=\gamma a_0, \tag{19}$$

using the determined value for $D_0/r_0^2$, and estimating $\nu=3\times10^{13}$/sec, one obtains $\gamma=3.5$. Thus, a value of 3.5

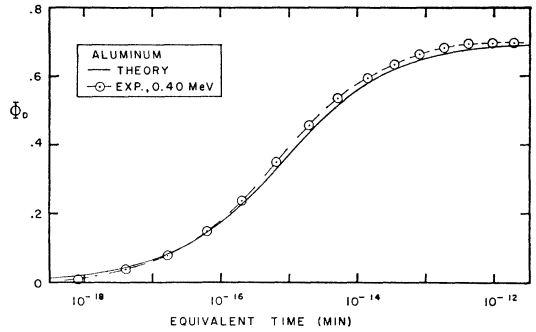


FIG. 4. The fractional recovery $\phi_D$ corresponding to the 0.40-MeV data from Fig. 1, plotted as a function of equivalent time $t_n$ and compared with theory.

lattice spacings is obtained for the capture radius $r_0$. Such a magnitude for the capture radius adds support to the concept of correlated diffusion.

The treatment of correlated recovery can be readily applied to other metals. Experimental data from thermal-neutron irradiated copper[14] is shown in Fig. 5 for values of $\phi_D$ versus temperature. The solid line represents the variation of $\phi_D$ when $\lambda=1.0$, $D_0/r_0^2=1.2\times10^{11}$/sec, and $E_m/k=1260$°K. By using Eqs. (18) and (19), and estimating $\gamma$ equal to 5, one obtains a value for $\nu$ of $3\times10^{12}$/sec. Previously, Corbett, Smith, and Walker[2,3] estimated values of $\gamma\simeq4$ and $\nu\simeq10^{12}$/sec so that these independent determinations give comparable results.

Values of $\lambda$ are quite sensitive to the irradiation energy as indicated in Table I. To account for this energy dependence, consider how an increase in the irradiation energy should increase the average distance which describes the separation of an interstitial from

[21] C. Wert and C. Zener, Phys. Rev. **76**, 1169 (1949).

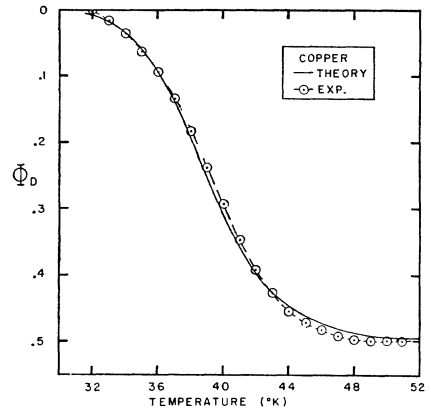


FIG. 5. The fractional recovery $\phi_D$ corresponding to the high-dose data from Fig. 4 of Ref. 14, compared with theory. The theoretical curve has been shifted $-\frac{1}{2}$°K along the temperature axis in accordance with the constant-rate-of-heating analysis, as explained in the text.

its vacancy. The average distance of separation can be calculated by using a radial distribution function. Specifically, the function

$$\Psi(r/r_0)=\{\exp[(1/\lambda)(1-r/r_0)]/\lambda(1+\lambda)\}(r/r_0) \tag{20}$$

is plotted in Fig. 6 for aluminum and in Fig. 7 for copper. Each function corresponds to an experimentally determined magnitude of $\lambda$ and these different functions show the effect of changing the irradiation energy. Quantitatively, the functions can be used to evaluate an average value for the vacancy-interstitial separation distance $\langle r\rangle$. Values for $\langle r\rangle$ are given in Table I. It is noted that for either metal, $\langle r\rangle$ has a magnitude as well as an energy dependence which is not unreasonable.

## IV. CONCLUSIONS

To describe the $I_D$ recovery, an analytic solution is derived for the problem of correlated recovery when the

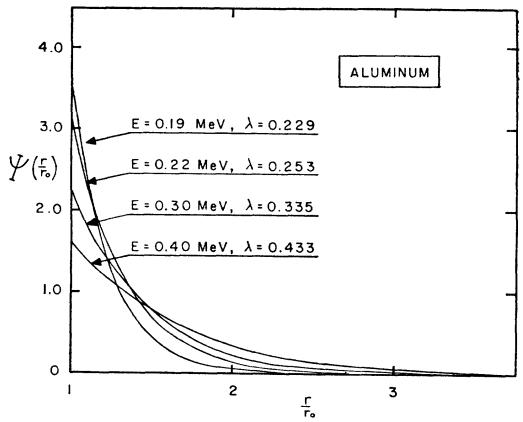


FIG. 6. Radial distribution function for the initial distribution of interstitials around their vacancies (excluding close pairs) for aluminum. $r_0$ is the capture radius for a freely migrating interstitial.

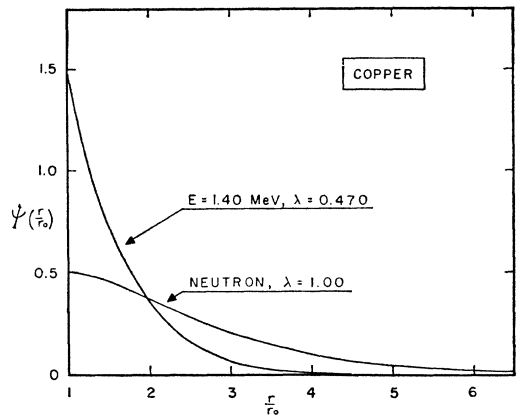


FIG. 7. Radial distribution function for the initial distribution of interstitials around their vacancies (excluding close pairs) for copper. $r_0$ is the capture radius for a freely migrating interstitial. The 1.40-MeV curve was evaluated by using data from Ref. 3.

initial distribution of the diffusing components is described by a modified exponential function. Previous solutions to this diffusion problem have been given by Fletcher and Brown[15] and by Waite.[16] Fletcher and Brown's work was based on a discrete initial distribution function. There is very little physical justification for using such a function to describe the initial distribution for the $I_D$ substage. The solution obtained by Waite (whose initial distribution was a Gaussian function) does not readily lend itself to a study of the energy dependence of correlated recovery. Both of these objections have been eliminated by deriving Eq. (12). This results gives information which is comparable to the solution by Waite's treatment because the annealing of defects is mainly dependent on the gross features of the initial distribution function.[16]

A consistent method for resolving the individual substages is required because some experimental measurements include annealing for adjacent recovery processes. The assumptions used to isolate the substages (i.e., the shape of $I_C$ is given by that of a first-order process and $I_E$ is symmetrical) present a realistic approach to evaluating the amount of recovery per substage. It is hoped that this procedure gives a more accurate evaluation than has been obtained by a previous technique.[20] But since there is no *a priori* means of resolving the recovery data, it is difficult to judge what errors are caused by either procedure.

When the experimental data for $\Phi_D$ is plotted versus temperature (see Fig. 3), the energy dependence of the $I_D$ substage is evident by the change in the rate of recovery and the amount of recovery. Both of these properties are readily explained by diffusion theory in terms of different magnitudes of $\lambda$. Each value for $\lambda$ characterizes a specific initial distribution that is associated with a given energy of irradiation. In order to judge these different distributions, a calculation is made of the average distance of separation between interstitials and vacancies. The average distances of separation have computed values which are self-consistent and therefore, support the interpretation of the $I_D$ substage in terms of correlated recovery.

The determination of $D_0/r_0^2$ and $E_m/k$ was obtained from the best fit between theoretical curves and experimental points. Values of these quantities for copper as determined from thermal neutron data are comparable to results obtained by Corbett, Smith, and Walker. The value of $D_0/r_0^2$ is used to estimate an approximate magnitude for the capture radius for interstitial-vacancy annihilation in aluminum. Finally, a calculation is made of the average value of the interstitial-vacancy separation distance $\langle r \rangle$, in terms of the capture radius, and the magnitude of $\langle r \rangle$ increases linearly with the irradiation energy. It is also noted how we have performed a preliminary analysis of the $I_E$ substage of aluminum in terms of Waite's[16] theory and that result gives confirmation of the numerical values of activation energy and $D_0/r_0^2$ which has been obtained from this work.[22]

## ACKNOWLEDGMENT

The authors are grateful to R. R. Coltman for detailed information about the results for the thermal neutron irradiation of copper.

[22] H. M. Simpson and R. L. Chaplin (unpublished).