Diffusion of Lattice Defects in a Stress Field

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The diffusion of lattice defects in a stress field produced by other defects such as dislocations, precipitates, or other point defects is considered. It is shown by calculation that in addition to the Einstein term which results from the force on the defect there is another term resulting from the influence of strain on the saddle-point configuration. This alters the migration energy. Detailed calculations for vacancy migration show that vacancy migration energies may be altered by 10%. The additional terms which should appear in the expression for the diffusion current are obtained. The diffusion equation is also modified by the appearance of additional terms, which are calculated. Finally, experimental evidence for changes in the migration energies of lattice vacancies, of divacancies, and of interstitials is described.

INTRODUCTION

THE object of this paper is to clarify the discussion concerning diffusion of point defects in a stress field. The traditional description first given by Einstein[1] supposes that the defect migrates in a potential $V(\mathbf{r})$ and that the elementary act of jumping over a migration barrier can be either assisted or resisted by the potential. The migration energy which results is

$$E_M+\mathbf{F}\cdot\tfrac{1}{2}\mathbf{a}, \tag{1}$$

where $\mathbf{F}$ is the force resulting from the potential and $\mathbf{a}$ is the vector distance between two neighboring equilibrium positions. This effect is well known.

There is also another effect which is not well known. Consider the elementary act of migration, i.e., consider an atomic jump: Let us examine vacancy migration in a fcc crystal, to be specific; actually, the argument is general but the geometrical details differ for each specific mechanism. The vacancy makes an atomic jump if an atom jumps through the rectangle shown in Fig. 1. The saddle-point configuration occurs when the moving atom is at the center of the rectangle. It is evident that a strain which increases the area of the rectangle will lower the migration barrier. Moreover, it is possible to imagine a strain field such that $V(\mathbf{r})$ is zero everywhere and yet which would have an influence on the barrier height. There are therefore two effects: One (the Einstein term) is associated with changes in the equilibrium defect energy with position; another (the barrier term) results because stress fields can alter the height of the activation barrier. Both effects are important.

ESTIMATES FOR VACANCY MIGRATION

If one considers a lattice vacancy in a fcc crystal, then $V(\mathbf{r})$ is determined by the pressure at $\mathbf{r}$. But one can lower the migration barrier by a strain field which has displacements as shown by the arrows in Fig. 1. This is just the type of strain field one expects at a vacancy which is in a ⟨110⟩ direction from an interstitial cluster at the origin in a fcc crystal. Let us calculate how large such effects can be. Consider lattice vacancies migrating in the stress field of an interstitial cluster in an isotropic elastic solid. The strains at distance r from the center of the cluster are[2]

$$\epsilon_{rr}=-2A/r^3, \qquad \epsilon_{\theta\theta}=\epsilon_{\phi\phi}=A/r^3, \tag{2}$$

where

$$A=vN_I/4\pi\Gamma. \tag{3}$$

Here N_I is the number of interstitials per cluster, and v is the volume increase which results when one interstitial is created in an infinite solid by inserting an atom into an interstitial site. Γ is the Eshelby surface correction [$\Gamma=3(1-\nu)/(1+\nu)\cong 1.5$, where ν is Poisson's ratio].

Consider a lattice vacancy which lies along a ⟨110⟩ direction which passes through the center of the interstitial cluster. We shall do our illustrative calculations for copper. Let us assume that the ion-ion interaction potential is that used by Huntington.[3] If we suppose that the change in the barrier height is given by the change in this closed-shell repulsion between the atom at the saddle point X in Fig. 1 and the four neighboring atoms, then

$$\Delta E_V{}^M=4V_0\left(e^{\alpha[r_0-(\rho+\Delta r)]/r_0}-e^{\alpha(r_0-\rho)/r_0}\right), \tag{4}$$

where for copper Huntington[3] suggests $V_0=0.053$ eV

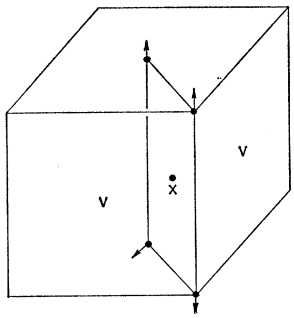

FIG. 1. The saddle-point configuration for vacancy diffusion in a fcc metal.

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[1] W. Jost, *Diffusion in Solids Liquids and Gases* (Academic Press Inc., New York, 1952), p. 139.
[2] A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, Inc., New York, 1944), 4th ed., p. 142.
[3] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

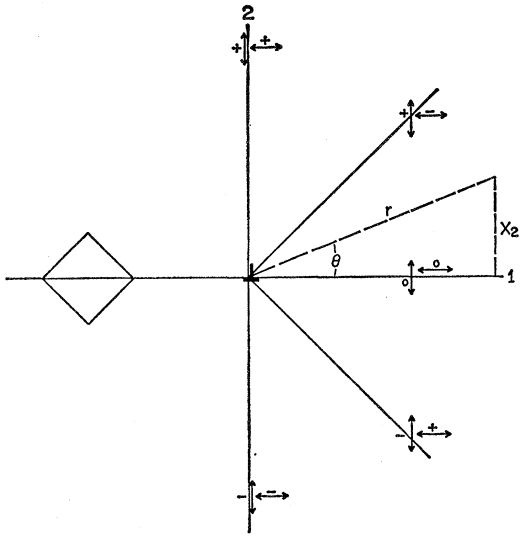

FIG. 2. Vacancy diffusion near an edge dislocation in a fcc metal. The double ended arrows show possible jump directions perpendicular to the dislocation axis. + means $\Delta E_V{}^M>0$. − means $\Delta E_V{}^M<0$. The cube axes are shown on the left.

and $\alpha=13.9$. Here r_0 is the equilibrium interatomic distance, ρ is the distance from the saddle-point atom to its four neighbors in the normal lattice ($\rho=r_0\sqrt{3}/2$), and Δr is the increase caused by the displacements near the interstitial cluster. One has

$$\Delta r=\rho(\tfrac{1}{2}\epsilon_{\theta\theta}{}^2+\tfrac{1}{4}\epsilon_{\phi\phi}{}^2)^{1/2}=r_0\sqrt{3}A/2r^3. \tag{5}$$

If there are 100 interstitials per cluster and if v is 2 atomic volumes, then

$$\Delta E_V{}^M=0.0162 \text{ eV} \quad \text{at } r=50 \text{ Å}, \ \Delta r=2.204\times10^{-3} \text{ Å}$$

and

$$\Delta E_V{}^M=0.125 \text{ eV} \quad \text{at } r=25 \text{ Å}, \ \Delta r=1.763\times10^{-2} \text{ Å}.$$

These are decreases in migration energy for jumps directly towards or away from the interstitial cluster. Vacancies jumping in a direction perpendicular to the radial direction experience a much smaller effect since the rectangle is compressed in the radial direction and expanded in the perpendicular direction. Note that this introduces an anisotropy into the jump rate (C. P. Flynn in unpublished work noted that external stresses change the diffusion constant to a diffusion tensor).

We should also calculate the equilibrium energy of the vacancy as a function of its position near the interstitial cluster using a discrete defect model. In this case, the influence of the interstitial cluster is to change the separation distances between the 12 atoms which are nearest neighbors of the vacancy. Actually, we should calculate these distance changes starting from a situation in which the 12 nearest neighbors have collapsed in towards the vacancy through a distance s. For a vacancy along a ⟨110⟩ direction from an interstitial cluster using Huntington's potential, the interaction between the cluster and the vacancy is

$$V(r)=8V_0e^{\alpha s/r_0}(e^{9\alpha As/2r^4}+e^{3\alpha As/2r^4}-2). \tag{6}$$

Thus, the change in $E_V{}^M$ resulting from the interaction is

$$\begin{aligned}\Delta E_V{}^M&=-(\partial V/\partial r)(a/\sqrt{2})\\&=(48V_0\alpha As a/\sqrt{2}r^5)e^{\alpha s/r_0}(3e^{9\alpha As/2r^4}+e^{3\alpha As/2r^4}).\end{aligned} \tag{7}$$

For a vacancy which is 25 Å from an interstitial cluster containing 100 interstitials, $\Delta E_V{}^M$ is 6.17×10^{-5} eV and thus, this effect is negligible. We took $s=0.021r_0=0.021a/\sqrt{2}$ in this calculation.

This model gives the vacancy migration energy in a perfect crystal to be

$$E_V{}^M=4V_0e^{+\alpha(r_0-\rho)/\rho}, \tag{8}$$

where the influence of any collapse around the vacancy in its equilibrium configuration has been neglected. For copper, using Huntington's soft potential, this gives $E_V{}^M=1.364$ eV, whereas the experimental value is 0.88 eV. If the four surrounding atoms are relaxed outward to $\rho+0.0300r_0$, the migration energy drops to 0.90 eV. The influence of strain on the migration energy can then be calculated in the manner described above, but using the relaxed saddle-point configuration. One finds that the unrelaxed $\Delta E_V{}^M s$ are decreased by the factor $E_V{}^M(\text{relaxed})/E_V{}^M(\text{rigid})=0.90/1.364=0.66$.

If one considers the diffusion of point defects near a dislocation since the stress fields are of long range, one should expect important effects. Consider, for example, an edge dislocation in an isotropic elastic fcc crystal. Assume that the dislocation lies along a ⟨001⟩ direction. For a whole dislocation the Burgers vector is $\frac{1}{2}a(1,1,0)$. The tensile strains perpendicular to the dislocation axis are[4] (see Fig. 2)

$$\begin{aligned}\epsilon_{11}&=-\frac{b}{2\pi}\frac{x_2}{r^2}\left[1+\frac{\cos2\theta}{2(1-\nu)}\right],\\ \epsilon_{22}&=+\frac{b}{2\pi}\frac{x_2}{r^2}\left[\frac{\nu}{1-\nu}+\frac{\cos2\theta}{2(1-\nu)}\right].\end{aligned} \tag{9}$$

In this system, vacancy jumps which occur in the plane normal to the dislocation axis can occur either parallel to **b** or perpendicular to it. The symmetry of the changes in $E_V{}^M$ are shown in Fig. 2, where + means that $\Delta E_V{}^M$ is positive. There are, of course, jumps which take place at 45° to the dislocation axis. Such jumps also have their migration energies altered, but the change is smaller than the changes seen in the 12 plane. In the 12 plane, the effects are largest at $\theta=45°$. In Eqs. (9), if we

[4] J. Friedel, *Dislocations* (Addison Wesley Publishing Co., Inc., Reading, Mass., 1964), p. 21.

take the square brackets equal to unity (as they are near 45°), then

$$\Delta r = r_0(\sqrt{\tfrac{3}{2}})(b/4\pi)(1/r). \quad (10)$$

For the fcc crystals, where $b=a/\sqrt{2}$, if $r=2.5\times10^{-7}$ cm,

$$\Delta r = 1.794\times10^{-2}\text{ Å}, \quad r=25\text{ Å}$$
$$\Delta r = 0.897\times10^{-2}\text{ Å}, \quad r=50\text{ Å}.$$

Thus, using Eq. (4), the magnitude of the changes in activation energy are for copper

$$\Delta E_V{}^M = (0.140\text{ eV})\times0.66 = 0.092\text{ eV} \quad (r=25\text{ Å}, \ \theta\cong45°)$$
$$\Delta E_V{}^M = (0.0683\text{ eV})\times0.66 = 0.0451\text{ eV} \quad (r=50\text{ Å}).$$

We have used $\nu=\frac{1}{3}$. The changes at $\theta=\pm90°$ are about one quarter of the changes at 45°. It is apparent, therefore, that the dislocation strains can have appreciable effect on $E_V{}^M$. Screw dislocations will also produce changes in $E_V{}^M$.

In general, the saddle-point configurations are planar. One can define unit vectors **i** and **j** along two lines joining the saddle-point position of the central moving atom and two noncollinear nearest neighbors. The strains which are important are ϵ_{ii} and ϵ_{jj}, the tensile strains along **i** and **j**. Linear combinations of **i** and **j** may also be involved. For example, if one has a saddle-point configuration which has the central atom at the middle of an equilateral triangle of atoms then ϵ_{ii}, ϵ_{jj}, and $\epsilon_{i+j,i+j}$ would be the important tensile strains. If the local strains are not too large, the change in the migration energy can be written

$$\Delta E_{ij} = \sum_l \text{grad}\phi_l\cdot\mathfrak{y}_l + \tfrac{1}{2}b(\mathbf{i}\times\mathbf{j})\cdot\text{grad}V, \quad (11)$$

where ϕ_l is the atom-atom interaction potential. $\mathfrak{y}_l$ is the change in the distance between the central atom and its lth nearest neighbor ($\mathfrak{y}_l=\mathbf{r}_l\epsilon_{ll}$, where $\mathbf{r}_l$ is the vector distance between the central atom and its lth nearest neighbor. The $\mathbf{r}_l$ used should be the relaxed value appropriate for migration in the unstrained crystal.) b is the atomic jump distance, and V is the potential energy of the defect. The sum is over all nearest neighbors of the central jumping atom. If one considers two successive atomic planes along a given jump direction, distinguished by the unit vector **h**, one finds that the diffusion current **J** is given by

$$\mathbf{J} = -\nu Nb^2 e^{-E_0/kT}\sum_h \mathbf{h}\left[\frac{\partial c}{\partial\rho_h}\left(1-\sum_l\frac{\text{grad}\phi}{kT}\cdot\mathfrak{y}_{lh}\right)+\frac{1}{kT}\frac{\partial V}{\partial\rho_h}\right], \quad (12)$$

where N is the number of atoms per unit volume, b is the jump distance, ρ_h is distance measured along the hth jump direction, ν is the atomic vibration frequency, and the sum over h is over all crystallographic jump directions. E_0 is the migration energy of the defect in a perfect crystal. If one considers three successive atomic planes perpendicular to a particular jump direction, one obtains the diffusion equation. It is

$$\frac{\partial c}{\partial t} = \nu b^2 e^{-E_0/kT}\sum_h\left[\frac{\partial^2 c}{\partial\rho_h{}^2}\left(1-\sum_l\frac{\text{grad}\phi}{kT}\cdot\mathfrak{y}_{lh}\right)-\frac{\partial c}{\partial\rho_h}\left(\sum_l\frac{\text{grad}\phi}{kT}\cdot\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h}-\frac{1}{kT}\frac{\partial V}{\partial\rho_h}\right)+\frac{c}{2kT}\frac{\partial^2 V}{\partial\rho_h{}^2}\right]. \quad (13)$$

Note that contributions from the alteration of the activation energy occur in both **J** and in the diffusion equation.

It is instructive to calculate orders of magnitude. For a given ⟨110⟩ direction in copper,

$$\sum_l\frac{\text{grad}\phi}{kT}\cdot\mathfrak{y}_{lh} = \frac{0.0107\text{ eV}}{0.02585\text{ eV}} = 0.414$$

for a vacancy which is 50 Å from an interstitial cluster containing 100 interstitials. T is 300°K. Thus, even at 50 Å from the cluster the expansion is not rapidly convergent. From Eq. (5), one finds with relaxation that

$$\tfrac{1}{2}b\sum_l\frac{\text{grad}\phi}{kT}\cdot\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h} = 0.06428,$$

so that this term in the expansion is not very large at 50 Å from the cluster and the expansion is justified. At 25 Å this term is sixteen times larger. This again shows the large influence of strains on the diffusion. If the exponentials are not expanded, one obtains

$$\mathbf{J} = -\nu Nb^2\sum_{\mathbf{h}}\mathbf{h}\left\{+\frac{\partial c}{\partial\rho_h}\cosh\left[\frac{b}{2kT}\left(\sum_l\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h}\cdot\text{grad}\phi-\frac{\partial V}{\partial\rho_h}\right)\right]\exp\left[-\left(E_0+\sum_l\mathfrak{y}_{lh}\cdot\text{grad}\phi-\frac{b^2}{4}\frac{\partial^2 V}{\partial\rho_h{}^2}\right)\Big/kT\right]\right.$$
$$-\frac{c}{b}\sinh\left[\frac{b}{2kT}\left(\sum_l\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h}\cdot\text{grad}\phi+\frac{\partial V}{\partial\rho_h}\right)\right]\exp[-(E_0+\sum_l\mathfrak{y}_{lh}\cdot\text{grad}\phi)/kT]$$
$$\left.-\frac{c}{b}\sinh\left[\frac{b}{2kT}\left(\sum_l\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h}\cdot\text{grad}\phi-\frac{\partial V}{\partial\rho_h}\right)\right]\exp\left[-\left(E_0+\sum_l\mathfrak{y}_{lh}\cdot\text{grad}\phi-\frac{b^2}{4}\frac{\partial^2 V}{\partial\rho_h{}^2}\right)\Big/kT\right]\right\}$$

and

$$\frac{\partial c}{\partial t}=\nu\sum_{h}\Bigg\{+b^2\frac{\partial^2 c}{\partial\rho_h^2}\cosh\Bigg[\frac{b}{2kT}\Big(\sum_l\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h}\cdot\mathrm{grad}\phi-\frac{\partial V}{\partial\rho_h}\Big)\Bigg]\exp\Bigg[-\Big(E_0+\sum_l\mathfrak{y}_{lh}\cdot\mathrm{grad}\phi-\frac{b^2}{4}\frac{\partial^2 V}{\partial\rho_h^2}\Big)\Big/kT\Bigg]$$

$$-2b\frac{\partial c}{\partial\rho_h}\sinh\Bigg[\frac{b}{2kT}\Big(\sum_l\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h}\cdot\mathrm{grad}\phi-\frac{\partial V}{\partial\rho_h}\Big)\Bigg]\exp\Bigg[-\Big(E_0+\sum_l\mathfrak{y}_{lh}\cdot\mathrm{grad}\phi-\frac{b^2}{4}\frac{\partial^2 V}{\partial\rho_h^2}\Big)\Big/kT\Bigg]$$

$$+2c\cosh\Bigg[\frac{b}{2kT}\Big(\sum_l\frac{\partial\mathfrak{y}_{lh}}{2\rho_h}\cdot\mathrm{grad}\phi-\frac{\partial V}{\partial\rho_h}\Big)\Bigg]\exp\Bigg[-\Big(E_0+\sum_l\mathfrak{y}_{lh}\cdot\mathrm{grad}\phi-\frac{b^2}{4}\frac{\partial^2 V}{\partial\rho_h^2}\Big)\Big/kT\Bigg]$$

$$-2c\cosh\Bigg[\frac{b}{2kT}\Big(\sum_l\frac{\partial\mathfrak{y}_{lh}}{\partial\rho_h}\cdot\mathrm{grad}\phi+\frac{\partial V}{\partial\rho_h}\Big)\Bigg]\exp\big[-(E_0+\sum_l\mathfrak{y}_{lh}\cdot\mathrm{grad}\phi)/kT\big]\Bigg\}\,.$$

These expressions are complicated, and as yet we have not used them to follow the evolution of a system as time goes on.

EXPERIMENTAL

In a series of recent papers, Sharma, Lee, and Koehler[5] have shown that lattice vacancies are responsible for the annealing which occurs just above room temperature in three different experiments in 99.999+% and 99.9999+% pure gold. Defects were produced by (a) fast quenching from 700°C, (b) electron irradiation at 100°K, and (c) a few percent extension at 4.2°K. The defect migrating during annealing was identified by determining its activation energy for migration by measuring the rate of annealing before and after a sudden temperature change. Figure 3 shows some of these data on 99.9999% gold and on 99.999% gold. The less pure gold shows some annealing before stage III begins. The activation energies measured by the slope change method are given along the curves. Note that the activation energies associated with this low-temperature annealing are lower than those associated with stage III. Shimomura[6] has shown that interstitial platelets exist below stage III in these electron irradiated gold specimens. He found that these interstitial clusters disappear during stage-III annealing. Shimomura observed that the number of such clusters does not change with the irradiation dose; the average size increases with dose. Moreover, he found that the cluster density is a function of purity; the 99.9999% pure specimens contain 8×10^{14} clusters per cm³, whereas the 99.999% specimens contain 1.8×10^{16} clusters per cm³. In the 99.9999% specimens, after 2.8×10^{18} electrons per cm² (3 MeV), the average diameter was about 60 Å. This cluster therefore contains about 396 interstitials. At a similar dose the clusters in the 99.999% specimens have an average diameter of something like 5.5 Å and contain only three or four interstitials.

The annealing which occurs below stage III in the 99.999% specimens results, we believe, from the migration of vacancies which are close to the interstitial clusters and hence experience a large reduction in migration energy. There is more of such annealing in a 99.999% specimen than in a 99.9999% specimen since a larger volume is affected. In attempting to use the theory given above for strains near interstitial clusters to establish this point we run into the following difficulty. The strains given in Eq. (2) assumed that the cluster was an oversized defect which is spherically symmetric. Actually the defects are platelike precipitates on the {111} planes. For calculations involving large strains, i.e., for vacancies close to the cluster, the shape of the cluster is important.

Meshii and Kauffman[7] have done the following interesting experiment on pure gold. They quenched from 1000°C and cooled quickly to 80°K where they plastically bent the specimen. The specimen was then annealed at −10, 0, 10°C, etc. The activation energies measured by slope change increased from 0.26 eV to 0.65±0.05 eV and for further annealing stayed at the 0.65-eV value. In this experiment one is probably observing divacancies migrating in the dislocation strain fields since Ytterhus and Balluffi[8] have shown that the divacancy migrates with an activation energy of 0.70 eV in gold.

In the case of interstitials one has clear evidence that the energy of migration of an interstitial is lowered if a lattice vacancy is nearby. In the stage-I annealing of irradiated copper and silver there are a number of close pair peaks which obey first-order annealing kinetics and then at a slightly higher temperature there is a second-order peak. The first-order peaks are commonly assigned to the recombination of close interstitial vacancy pairs. The second-order process is assigned to long-range migration of the interstitial. In copper and in silver, Palmer, Magnuson, and Koehler[9] assign

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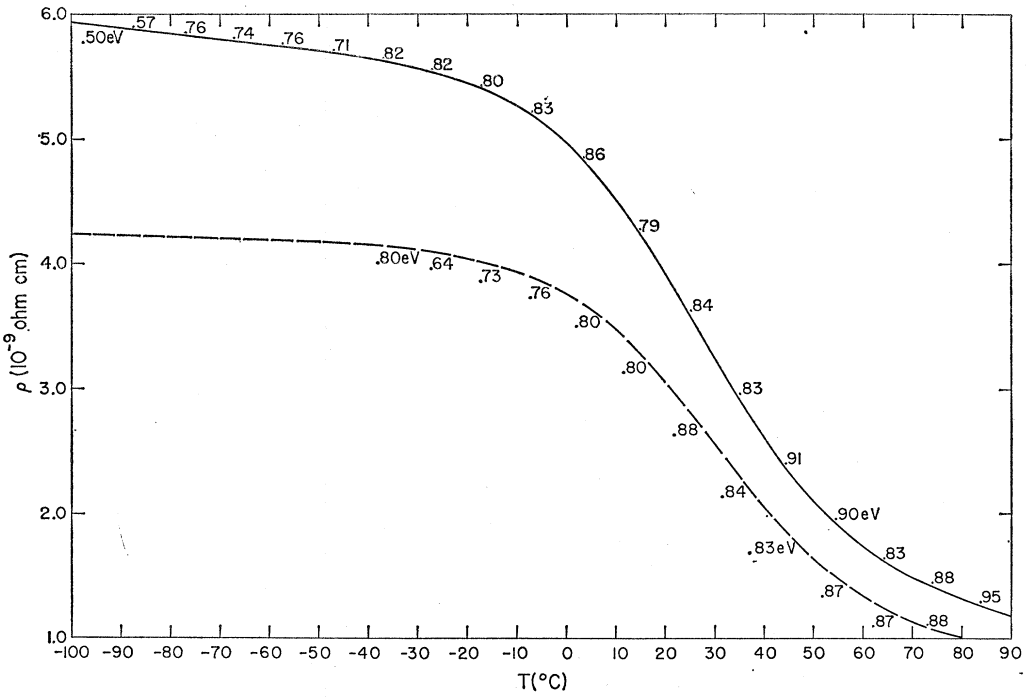

FIG. 3. The annealing of pure Au electron irradiated at 100°K. Full line gives data for 99.999% pure Au; dashed line gives data for 99.9999% pure Au. Activation energies determined by slope change at the temperatures shown (for example 0.50 eV by change from −100 to −90°C) are displayed along the isochronal annealing curves. Time at each temperature, 32 min; temperatures, 10°C apart.

activation energies as follows:

	E_A	E_B	E_C	E_D	E_E
Cu	0.048 eV	0.080	0.092	0.112	0.120±0.005 eV
Ag		0.045	0.060	0.080 eV.	

The 0.120-eV value was obtained for stage I_E by Corbett and Walker[10] who believe that I_D and I_E are associated with the same activation energy. Granato and Nilan[11] believe that I_D and I_E have different activation energies. Thus in copper the presence of a nearby vacancy lowers the migration energy of an interstitial by as much as 0.07 eV (for E_A). Moreover the interstitial and vacancy are probably separated by a distance greater than approximately 4 Å since theoretical calculations show that for smaller separations spontaneous recombination occurs.[12]

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[12] M. Doyama and R. M. J. Cotterill, Phys. Rev. **137**, A994 (1965); L. Tewordt, *ibid.* **109**, 61 (1958).

CONCLUSIONS

We have attempted to show by rather rough calculations that defect migration energies are altered by the strain fields near other defects such as dislocations and clusters of interstitial atoms. The important changes which are produced in the diffusion equations are described. Finally, experimental evidence for the influence of strain fields on the migration energies of vacancies, divacancies, and interstitials, is given.

The calculations made here should be repeated using the strain fields appropriate for an elastically anisotropic solid. The point of view adopted here is similar to that of Overhauser,[7] but he discussed averaged values rather than considering the detailed spatial variation.

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