

yield stress for the 0°K isotherm, and an equation of the type<sup>13,11,2</sup>

$$P_H = C_0^2(V_0 - V) / [V_0 - S_0(V_0 - V)]^2 \quad (16)$$

for the volume dependence of the Hugoniot pressure. The values of the parameters in this equation were taken from McQueen and Marsh<sup>2</sup>:  $C_0 = 0.3243$  cm/ $\mu$ sec,  $S_0 = 1.586$ ; the better agreement with these authors' data is obtained assuming zero yield stress, but the initial value for  $\gamma$ , 2.71, is too high.

#### 4. CONCLUSION

The results obtained using the closed-shell repulsive potential proposed by Koehler and Duvall are in very good agreement with the experimental data on the

<sup>13</sup>L. V. Al'tshuler, K. K. Krupnikov, and M. I. Brazhnik, *Soviet Phys.—JETP* **7**, 614 (1958); L. V. Al'tshuler, K. K. Krupnikov, B. N. Ledenev, V. L. Shuchikhin, and M. I. Brazhnik, *ibid.* **7**, 606 (1958).

shock wave compression of silver. Though the assumption of zero yield stress gives a slightly better agreement with the experimental data, the introduction of a nonzero yield stress presents some points of interest, such as the stressed influence of the Fermi energy term, and further exploration of this possibility would perhaps be worthwhile.

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## Diffusion of Single Vacancies and Divacancies in Quenched Gold\*

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An effective diffusion coefficient  $D_{\text{eff}}$ , and an effective energy of migration  $E_m$  are derived which describe the combined diffusion of single vacancies and divacancies which are in thermal equilibrium.  $D_{\text{eff}}$  is the appropriate diffusion "constant" to be used in Fick's law, if one wishes to describe the flow of voids, and expresses the fact that each vacancy during its random walk spends part of its lifetime as a single vacancy and part of its lifetime as a divacancy.  $E_m$  can be expressed in terms of  $E_m^1$  and  $E_m^2$  (the energies of migration of a single vacancy and a divacancy, respectively), and is concentration- and temperature-dependent. Its minimum is  $E_m^2 - B_2$ , where  $B_2$  is the binding energy of a divacancy. From analysis of measurements of  $E_m$  on Au specimens quenched from above 800°C, one finds that  $E_m^2 - B_2 \sim 0.56$  eV, or more directly that  $E_m^1 + B_2 - E_m^2 = 0.26 \pm 0.03$  eV. The same value for this latter parameter was derived from another independent experiment, namely from the critical concentration of vacancies for which clustering will just occur.

The binding energy of a divacancy in Au was observed to be:  $B_2 = 0.10 \pm 0.03$  eV, and its energy of migration:  $E_m^2 = 0.66 \pm 0.06$  eV.  $B_2$  was obtained from an analysis of the decrease in resistivity observed during the transient process in which single vacancies and divacancies come into equilibrium with one another. In addition it was found that the resistivity of a divacancy is  $(4.6 \pm 3)\%$  less than that of two well-separated single vacancies.

#### I. INTRODUCTION

**G**OLD was quenched from high temperatures and annealed in the vicinity of room temperature by Bauerle and Koehler.<sup>1</sup> Specimens quenched from 700°C annealed by a first-order annealing process. The energy of migration was 0.82 eV and about  $10^6$  jumps were required to reach the sinks. The quenched in lattice vacancies anneal out at existing dislocations.

They observed a much lower energy of migration during annealing if the specimens were quenched from 800°C or above. For a specimen quenched from 800°C,  $E_m = 0.66 \pm 0.03$  eV; after a 925°C quench  $E_m = 0.63 \pm 0.06$  eV; and after a 1000°C quench  $E_m = 0.60 \pm 0.04$  eV. Koehler, Seitz, and Bauerle<sup>2</sup> attributed this to the presence of divacancies which are in thermal equilibrium with single vacancies. They defined an effective diffusion constant which we shall elaborate in this paper in detail, experimentally and theoretically.

Koehler, Seitz, and Bauerle<sup>2</sup> made a first attempt to

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<sup>1</sup> J. E. Bauerle and J. S. Koehler, *Phys. Rev.* **107**, 1493 (1957).

<sup>2</sup> J. S. Koehler, F. Seitz, and J. E. Bauerle, *Phys. Rev.* **107**, 1499 (1957).

describe the life history of vacancies in gold. In this and the next paper, some of their basic ideas are examined in more detail. In addition the wealth of new experimental information available in the last few years enables additional conclusions to be drawn. Moreover, because of better insight into the nature of the defects involved, more specific experiments can be designed.

The general set of differential equations, which govern the kinetics for single, di-, tri-, and tetra-vacancies are

$$\begin{aligned} dc_1/dt = & -2\alpha_1c_1^2 + 2\alpha_2c_2 - \beta_1c_1c_2 + \beta_2c_3^{60} - \gamma_1c_1c_2 \\ & + \gamma_2c_3^{90} - \delta_1c_1c_2 + \delta_2c_3^{90} - 3\epsilon_1c_1^3 + 3\epsilon_2c_3^{120} \\ & - \zeta_1c_1c_2 + \zeta_2c_3^{120} - \eta_1c_1c_2 + \eta_2c_3^{120} - 3\theta_1c_1^3 + 3\theta_2c_3^{120} \\ & - \kappa_1c_1c_2 + \kappa_2c_3^{180} - \lambda_1c_1c_2 + \lambda_2c_3^{180} - 3\mu_1c_1^3 + 3\mu_2c_3^{180} \\ & - \chi_1c_1c_3^{60} + D_1\nabla^2c_1, \quad (1a) \end{aligned}$$

$$\begin{aligned} dc_2/dt = & +\alpha_1c_1^2 - \alpha_2c_2 - \beta_1c_1c_2 + \beta_2c_3^{60} \\ & - \gamma_1c_1c_2 + \gamma_2c_3^{90} - \delta_1c_1c_2 + \delta_2c_3^{90} - \zeta_1c_1c_2 + \zeta_2c_3^{120} \\ & - \eta_1c_1c_2 + \eta_2c_3^{120} - \kappa_1c_1c_2 + \kappa_2c_3^{180} - \lambda_1c_1c_2 + \lambda_2c_3^{180} \\ & - 2\xi_1c_2^2 + D_2\nabla^2c_2, \quad (1b) \end{aligned}$$

$$\begin{aligned} dc_3^{60}/dt = & +\beta_1c_1c_2 - \beta_2c_3^{60} + \pi_1c_3^{90} - \pi_2c_3^{60} \\ & + \sigma_1c_3^{120} - \sigma_2c_3^{60} - \chi_1c_1c_3^{60}, \quad (1c) \end{aligned}$$

$$\begin{aligned} dc_3^{90}/dt = & \gamma_1c_1c_2 - \gamma_2c_3^{90} + \delta_1c_1c_2 - \delta_2c_3^{90} \\ & + \epsilon_1c_1^3 - \epsilon_2c_3^{90} + \pi_2c_3^{60} - \pi_1c_3^{90} + \varphi_1c_3^{120} \\ & - \varphi_2c_3^{90} + D_3^{90}\nabla^2c_3^{90}, \quad (1d) \end{aligned}$$

$$\begin{aligned} dc_3^{120}/dt = & \zeta_1c_1c_2 - \zeta_2c_3^{120} + \eta_1c_1c_2 - \eta_2c_3^{120} + \theta_1c_1^3 \\ & - \theta_2c_3^{120} - \sigma_1c_3^{120} + \sigma_2c_3^{60} - \varphi_1c_3^{120} + \varphi_2c_3^{90} \\ & + \psi_1c_3^{180} - \psi_2c_3^{120} + D_3^{120}\nabla^2c_3^{120}, \quad (1e) \end{aligned}$$

$$\begin{aligned} dc_3^{180}/dt = & \kappa_1c_1c_2 - \kappa_2c_3^{180} + \lambda_1c_1c_2 - \lambda_2c_3^{180} + \mu_1c_1^3 \\ & - \mu_2c_3^{180} + \psi_2c_3^{120} - \psi_1c_3^{180}, \quad (1f) \end{aligned}$$

$$dc_4/dt = \chi_1c_1c_3^{60} + \xi_1c_2^2. \quad (1g)$$

A detailed description of the derivation of the equations for the tri- and tetra-vacancies will be given in our next paper<sup>3</sup> (to be referred to as Paper II). They are included here, because these complexes cannot always be neglected in the case of high-temperature quenches.  $c_1$  and  $c_2$  are the concentrations of single and divacancies;  $c_3^{90}$ ,  $c_3^{120}$ ,  $c_3^{180}$ , and  $c_3^{60}$  are the concentrations of four different configurations of trivacancies (see Paper II);  $c_4$  is the concentration of tetravacancies. The various rate constants are indicated by Greek letters and listed in Table I together with the process they describe and the defect that migrates in performing the reaction. The subscripts 1 and 2 refer to formation and dissociation, respectively.  $\nu_1$ ,  $\nu_2$ ,  $\nu_2'$ , and  $\nu_3$  are the frequencies of vibration of an atom next to a vacancy, a common neighbor of both members of two divacancy, a common neighbor of two of the three trivacancy members, and a common neighbor of all the vacancies of a trivacancy, respectively;  $E_m^1$ ,  $E_m^2$ ,  $E_m^{2'}$ , and  $E_m^3$  are the corresponding energies of migration.  $B_2$ ,  $B_3^{60}$ ,  $B_3^{90}$ ,

<sup>3</sup> M. De Jong and J. S. Koehler, following paper [Phys. Rev. 129, 49 (1963)].

TABLE I. The rate constants for the formation and the dissociation of single, di-, tri-, and tetra-vacancies.<sup>a</sup>

Description	Reaction	Migrating defect
$\alpha_1 = 84\nu_1e^{-E_m^1/kT}$		
$\alpha_2 = 14\nu_1e^{-(E_m^1+B_2)/kT}$	$s+s \rightleftharpoons d$	$s$
$\beta_1 = 20\nu_1e^{-E_m^1/kT}$		
$\beta_2 = 15\nu_1e^{-(E_m^1+B_3^{60})/kT}$	$s+d \rightleftharpoons t^{60}$	$s$
$\gamma_1 = 8\nu_2e^{-E_m^2/kT}$		
$\gamma_2 = 4\nu_2e^{-(E_m^2+B_3^{90})/kT}$	$s+d \rightleftharpoons t^{90}$	$d$
$\delta_1 = 24\nu_1e^{-E_m^1/kT}$		
$\delta_2 = 12\nu_1e^{-(E_m^1+B_3^{90})/kT}$	$s+d \rightleftharpoons t^{90}$	$s$
$\epsilon_1 = 48\nu_1e^{-E_m^1/kT}$		
$\epsilon_2 = 4\nu_1e^{-(E_m^1+B_3^{90}+B_2)/kT}$	$s+s+s \rightleftharpoons t^{90}$	$s$
$\zeta_1 = 24\nu_2e^{-E_m^2/kT}$		
$\zeta_2 = 6\nu_2e^{-(E_m^2+B_3^{120})/kT}$	$s+d \rightleftharpoons t^{120}$	$d$
$\eta_1 = 56\nu_1e^{-E_m^1/kT}$		
$\eta_2 = 14\nu_1e^{-(E_m^1+B_3^{120})/kT}$	$s+d \rightleftharpoons t^{120}$	$s$
$\theta_1 = 72\nu_1e^{-E_m^1/kT}$		
$\theta_2 = 3\nu_1e^{-(E_m^1+B_3^{120}+B_2)/kT}$	$s+s+s \rightleftharpoons t^{120}$	$s$
$\kappa_1 = 14\nu_1e^{-E_m^1/kT}$		
$\kappa_2 = 14\nu_1e^{-(E_m^1+B_3^{180})/kT}$	$s+d \rightleftharpoons t^{180}$	$s$
$\lambda_1 = 8\nu_2e^{-E_m^2/kT}$		
$\lambda_2 = 8\nu_2e^{-(E_m^2+B_3^{180})/kT}$	$s+d \rightleftharpoons t^{180}$	$d$
$\mu_1 = 12\nu_1e^{-E_m^1/kT}$		
$\mu_2 = 2\nu_1e^{-(E_m^1+B_3^{180}+B_2)/kT}$	$s+s+s \rightleftharpoons t^{180}$	$s$
$\xi_1 = \xi_1\nu_2e^{-E_m^2/kT}$	$d+d \rightleftharpoons \text{tetravac.}$	$d$
$\pi_1 = 4\nu_2'e^{-E_m^{2'}/kT}$		
$\pi_2 = 6\nu_2'e^{-(E_m^{2'}+B_3^{90}-B_3^{90})/kT}$	$t^{60} \rightleftharpoons t^{90}$	$t$
$\sigma_1 = 2\nu_2'e^{-E_m^{2'}/kT}$		
$\sigma_2 = 6\nu_2'e^{-(E_m^{2'}+B_3^{60}-B_3^{120})/kT}$	$t^{60} \rightleftharpoons t^{120}$	$t$
$\chi_1 = 12\nu_1e^{-E_m^1/kT}$	$s+t^{60} \rightarrow \text{tetravac.}$	$s$
$\varphi_1 = 2\nu_2'e^{-E_m^{2'}/kT}$		
$\varphi_2 = 4\nu_2'e^{-(E_m^{2'}+B_3^{90}-B_3^{120})/kT}$	$t^{90} \rightleftharpoons t^{120}$	$t$
$\psi_2 = 2\nu_2'e^{-E_m^{2'}/kT}$		
$\psi_2 = 8\nu_2'e^{-(E_m^{2'}+B_3^{120}-B_3^{180})/kT}$	$t^{120} \rightleftharpoons t^{180}$	$t$
$D_1 = a^2\nu_1e^{-E_m^1/kT}$		
$D_2 = \frac{1}{8}a^2\nu_2e^{-E_m^2/kT}$		
$D_3^{90} = D_3^{120} = d_{30}a^2\nu_3e^{-E_m^3/kT}$		

<sup>a</sup>  $s$  = single vacancy,  $d$  = divacancy, and  $t$  = trivacancy.

$B_3^{120}$ , and  $B_3^{180}$  are the decrease in energy when two well-separated vacancies, or a vacancy and a divacancy, combine to form a divacancy, a 60°, 90°, 120°, and 180° trivacancy, respectively.  $k$  and  $T$  have the usual meaning.

The last term in Eqs. (1a), (1b), (1d), and (1e) describes the diffusion of the defect to the sinks.  $D_1$ ,  $D_2$ ,  $D_3^{90}$ , and  $D_3^{120}$  are the diffusion constants for single, di-, and trivacancies.

Even this set of equations is simplified and by no means complete. The frequency factors used are drastically reduced; in fact nearly all the various formation

and dissociation processes should be described by different sets of  $\nu$  and  $E_m$ . Eqs. (1) become even more complex if the interaction between vacancies and impurities are included. Moreover no long-range interaction between defects is included. This may be a serious oversimplification when dislocations are involved.

The coupled set of differential equations cannot be integrated in a straightforward manner. One can solve them on a computer using numerical values for the parameters as done by Dienes and Damask,<sup>4</sup> and Meshii, Mori and Kauffman.<sup>5</sup> This procedure has the disadvantage that one gains only little insight into the crucial parameters which control certain processes. On the other hand one can sometimes arrange matters, theoretically or experimentally, so that only a few terms have to be considered, thus giving a detailed picture of the behavior of the defects in special situations. One may then hope that one is able to integrate the simplified differential equations exactly. We will follow the last method.

## II. THEORY

In this section we shall consider the effective diffusion constant for vacancies when both single vacancies and divacancies contribute. It will be shown that this concept is useful in describing the wide range of energies of migration measured by Bauerle and later by Palmer.<sup>6</sup>

Koehler, Seitz, and Bauerle<sup>2</sup> pointed out that in gold since the binding energy  $B_2$  of the divacancy is small, at high vacancy concentrations a single vacancy will spend a fraction of its life as a single and the remainder as a divacancy. Hence in the diffusion process involving lattice vacancies one should use an effective diffusion constant  $D$ , which is

$$D = (D_1\tau_1 + 4D_2\tau_2) / (\tau_1 + 4\tau_2). \quad (2)$$

The four occurs because the gradients under which singles and divacancies diffuse are coupled by the equilibrium condition as we will show below. Here  $D_1 = \nu_1 a^2 e^{-E_m/kT}$  is the diffusion constant for single vacancies;  $D_2 = \frac{1}{2} \nu_2 a^2 e^{-E_m^2/kT}$  is the diffusion constant for divacancies;  $1/\tau_1 = \alpha_1 c_1$  (see Table I) gives the average lifetime  $\tau_1$  of a single. In pure metal, a single vacancy lives until it encounters another single forming a divacancy.  $1/\tau_2 = \alpha_2$  gives the average lifetime  $\tau_2$  of a divacancy which dies when it dissociates into two single vacancies. Hence,

$$D = \nu_1 a^2 e^{-E_m/kT} \left[ \frac{1 + 3(\nu_2/\nu_1)c_1 e^{(E_m^2 + B_2 - E_m^2)/kT}}{1 + 24c_1 e^{B_2/kT}} \right]. \quad (3)$$

If only single vacancies and divacancies diffuse and if the vacancies and divacancies maintain their local

equilibrium ratio, then  $D$  is the appropriate diffusion "constant" which must be used in Fick's law, if we wish to describe the flow of voids. This can be seen as follows: Let  $z$  be the local void concentration, i.e.,

$$z = c_1 + 2c_2. \quad (4)$$

Suppose a gradient exists in  $z$  in the  $x$  direction. Then what are the corresponding gradients in  $c_1$  and  $c_2$ ? If the singles and divacancies are in relative equilibrium, then it follows from Eq. (1a):

$$c_2 = 6c_1^2 e^{B_2/kT}. \quad (5)$$

The flux of voids which results from single-vacancy motion is obtainable in terms of the gradient of  $z$  using (4) and (5).

$$D_1 \frac{\partial c_1}{\partial x} = \nu_1 a^2 e^{-E_m/kT} \frac{\partial z}{\partial x} / [1 + 24c_1 e^{B_2/kT}].$$

Similarly, the flux of voids as divacancies is

$$2D_2 \frac{\partial c_2}{\partial x} = 24D_2 c_1 \frac{\partial c_1}{\partial x} e^{B_2/kT} = \frac{3\nu_2 a^2 c_1 e^{(-E_m^2 + B_2)/kT}}{1 + 24c_1 e^{B_2/kT}} \frac{\partial z}{\partial x}.$$

And adding these we obtain the total flux of voids  $J_z$ . We find that Fick's law is obeyed, i.e.,

$$J_z = -D \partial z / \partial x, \quad (6)$$

where  $D$  is given by (3). Note that  $D$  is concentration dependent.

The differential equation describing the diffusion of the voids is nonlinear, i.e.,

$$\partial z / \partial t = \text{div}(D \text{grad} z), \quad (7)$$

where  $D$  is a function of  $z$ . Although this equation can be separated approximately in the case voids annealing at dislocations, we have not been able to integrate the resulting nonlinear ordinary differential equation. Instead one can correlate the effective energies of motion  $E_m$  obtained by measuring the ratio of the rates of annealing at two temperatures at constant defect concentration, with the temperature dependence of  $D$ . It is assumed that the average vacancy concentration is the appropriate value to use in  $D$  for this comparison. Thus

$$\ln \frac{D(T_2)}{D(T_1)} = \ln \left[ \frac{\text{rate}(T_2)}{\text{rate}(T_1)} \right] = \frac{E_m}{k} \left( \frac{1}{T_1} - \frac{1}{T_2} \right). \quad (8)$$

Note that  $E_m$  defined in this way is concentration as well as temperature dependent. Another interesting point which follows from expressions (3) and (8) is that for the case that the second term in the numerator of (3) dominates, i.e., for high vacancy concentrations, one will not measure the energy of migration for divacancies  $E_m^2$ , but a lower value, namely  $E_m^2 - B_2$ . Finally, a measurement of  $E_m$  enables us to determine  $E_m^1 + B_2 - E_m^2$ , assuming that  $E_m^1$  is known and that the

<sup>4</sup> G. J. Dienes and A. C. Damask, Disc. Faraday Soc. **31**, 29 (1962).

<sup>5</sup> M. Meshii, T. Mori, and J. W. Kauffman, Phys. Rev. **125**, 1239 (1962).

<sup>6</sup> W. Palmer and J. S. Koehler, Bull. Am. Phys. Soc. **3**, 366 (1958).

second term in the denominator of (3) can be neglected. This is the case if the temperatures  $T_1$  and  $T_2$  are not too far apart ( $\leq 20^\circ\text{C}$ ).

The concepts given so far can be easily extended to the motion of vacancy-impurity clusters and trivacancies. The first group is not of interest here. The contribution of the migration of trivacancies can be neglected as will be discussed extensively in Sec. VII.

### III. EXPERIMENTAL PROCEDURE

The specimen material was 99.999% pure polycrystalline gold wire of 0.016-in. diam. The ratio of resistance at room temperature to that at  $4.2^\circ\text{K}$  ranged from 1800 to 3800. The wires were always annealed for 15 min at  $1000^\circ\text{C}$  prior to each run. The potential leads were 0.002-in. Au wire spotwelded to the wire at about 4 cm apart. The resistivity was directly measured at liquid helium temperature by conventional methods. The accuracy was  $\pm 10^{-11}$   $\Omega\text{cm}$ . Quenching was performed by immersing the wires in a liquid bath; water +10% NaCl was used for quenches to room temperature; water +29% CaCl<sub>2</sub> for quenches to  $-35^\circ\text{C}$ . Annealing was carried out in a water or alcohol bath controlled to  $\pm 0.01^\circ\text{C}$ .

### IV. RESULTS

#### A. The Effective Energy of Motion

In the case of quenches of gold from above  $800^\circ\text{C}$ , Bauerle and Koehler<sup>1</sup> determined energies of motion  $E_m$  only in a limited region of the annealing curve. Here, an attempt is made to follow the behavior of  $E_m$  from the beginning of the annealing process to the very end. Figure 1(a) shows the result for an Au wire quenched from  $900^\circ\text{C}$  and alternately annealed at 30 and  $40^\circ\text{C}$ .  $E_m$  at each point of temperature change was calculated according to Eq. (8). The rates of annealing at  $T_1$  and  $T_2$  to be used were determined by a more refined technique than applied previously,<sup>1</sup> namely, one in which all the measuring points were used to determine the rate of annealing at each point of temperature change.<sup>7</sup> Rate ( $T_1$ ) and rate ( $T_2$ ) are given by  $(d\ln\rho/dt)_1$  and  $(d\ln\rho/dt)_2$ , respectively. From the curve in Figure 1(a), one determines now  $(\ln\rho_2 - \ln\rho_1)/(t_2 - t_1)$  for each pair of subsequent measuring points ( $\rho_1$  and  $\rho_2$  are the resistivities at time  $t_1$  and  $t_2$ ).<sup>8</sup> By plotting this against  $(t_1 + t_2)/2$ , one obtains two smooth curves, one representing the rate of annealing at temperature  $T_1$ , and one for  $T_2$  (Fig. 1(b)). The resulting effective energies of migration  $E_m$  calculated at some points of the curves are indicated in the figure.  $E_m$  increases from 0.55 to 0.69 eV as annealing proceeds, i.e., as the void concentration decreases.

<sup>7</sup> We are indebted to Mr. W. Palmer who invented this method.

<sup>8</sup> In order to correct for the part of the resistivity that cannot be annealed out, the values of  $\rho$  given by  $\rho = f\rho_0$  were used, where  $f$  is defined by  $f = [\rho - \rho(\infty)]/[\rho_0 - \rho(\infty)]$  (see Paper II).

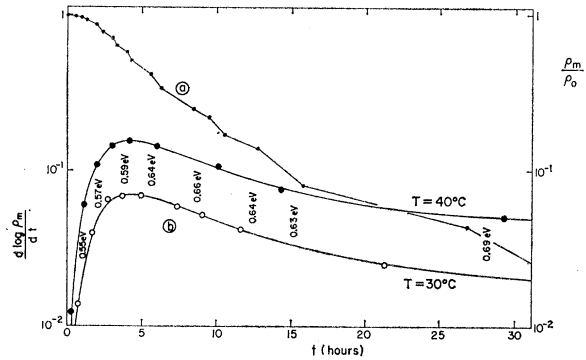


FIG. 1(a). The relative change of resistivity  $\rho/\rho_0$  with time  $t$ , for a gold specimen quenched from  $900^\circ\text{C}$  and annealed alternately at 30 and  $40^\circ\text{C}$ . (b). The annealing rate  $d\ln\rho/dt$  as a function of time.

#### B. Annealings Involving Only Single and Divacancies

In the experiment described under *A*, besides single and divacancies, higher vacancy-complexes also will be present, as briefly reported earlier. Palmer and Koehler<sup>6</sup> attempted to carry out experiments in which one only deals with single vacancies and divacancies, and no clustering of voids occurs. This can be accomplished if a divacancy breaks up before encountering another defect. If  $\tau_3$  is the average time required for a divacancy to encounter a single vacancy, then  $1/\tau_3 = (\gamma_1 + \zeta_1)c_1$ . Thus, no clusters are formed if  $\tau_3 > \tau_2$ , i.e., if

$$1 > \frac{16\nu_2}{7\nu_1} c_1 e^{(E_m^1 + B_2 - E_m^2)/kT}. \quad (9)$$

Here, one avoids clusters if  $c_1$  is small or if the annealing temperature is high. Palmer quenched gold wires from  $800^\circ\text{C}$  and annealed them alternately at 88 and  $98^\circ\text{C}$ . The initial energy of migration was found to be 0.73 eV for a quenched in resistivity of  $8 \times 10^{-9}$   $\Omega\text{cm}$ ; it increased gradually to 0.77 eV after 80% was annealed out. Unfortunately, the resistivity at infinite annealing times,  $\rho_r(\infty)$ , which is a sensitive test for the presence of clusters, is not known for his run. Therefore, we repeated his experiment, which revealed almost the same activation energies for migration, and gave  $\rho_r(\infty)/\rho_0 = 0 \pm 0.1\%$ . Indeed, clustering was negligible in this experimental arrangement.

#### C. The Binding Energy of a Divacancy

Up to now, no direct measurements of the binding energy  $B_2$  or the energy of motion  $E_m^2$  of divacancies in gold are available. A combination of the two, namely,  $E_m^1 + B_2 - E_m^2$  can be deduced from several experiments. (See Sec. V). We were not able to design an experiment in which  $E_m^2$  can be measured directly as done in the case of silver.<sup>9</sup> To perform such an experiment, the aver-

<sup>9</sup> M. Doyama and J. S. Koehler, Phys. Rev. **127**, 21 (1962).

age lifetime of a divacancy  $\tau_2$  has to be long compared with the average time  $t$  it takes a divacancy to reach a sink. Hence,

$$14\nu_1 e^{-(E_m^1+B_2)/kT} < 2D_2/x^2, \quad (10)$$

where  $2x$  is the average spacing of sinks. Assuming the highest sink concentration observed<sup>10</sup> ( $\sim 2 \times 10^{15}$  per  $\text{cm}^2$ ) and  $E_m^1+B_2-E_m^2=0.26$  eV, the above condition is fulfilled for  $T < 100^\circ\text{K}$ . At this temperature, annealing is too slow to measure. Another possibility is to study the transient process during which single vacancies and divacancies come into equilibrium with one another. This gives information from which the binding energy of a divacancy  $B_2$  can be calculated. One may hope to measure a small change of resistivity during this process if the resistivity of a divacancy differs from that of two singles. Therefore, a gold wire was quenched from  $1000^\circ\text{C}$  into a water + 29%  $\text{CaCl}_2$  bath at  $-35^\circ\text{C}$ . Using this low-temperature quenching bath, most of the quenched-in vacancies will be singles,<sup>11</sup> while recombination into divacancies takes about a day. During a subsequent anneal at  $-3^\circ\text{C}$ , an initial decrease in resistivity  $\Delta\rho$  was found which was superimposed on the normal annealing curve (Fig. 2). The decay time of this initial drop in resistivity was about 22 min. The total relative change in resistivity  $\Delta\rho_0/\rho_0$  is:

$$\Delta\rho_0/\rho_0 = (4.75 \pm 0.2) \times 10^{-3}$$

for a quenched-in resistivity of  $\rho_0 = 6.6 \times 10^{-8} \Omega\text{cm}$ . By annealing at  $-10.5^\circ\text{C}$ , the results were:

$$\Delta\rho_0/\rho_0 = (6.6 \pm 0.2) \times 10^{-3}$$

for  $\rho_0 = 4.8 \times 10^{-8} \Omega\text{cm}$ , and the process took about 70 min. In order to decide whether this initial drop of resistivity was due to the establishment of equilibrium between singles and divacancies, two additional experiments were performed: 1) Instead of quenching at  $-35^\circ\text{C}$ , a wire was quenched into the salt bath at  $+18^\circ\text{C}$ , held there for 5 min in order to obtain equilibrium between singles and divacancies, and sub-

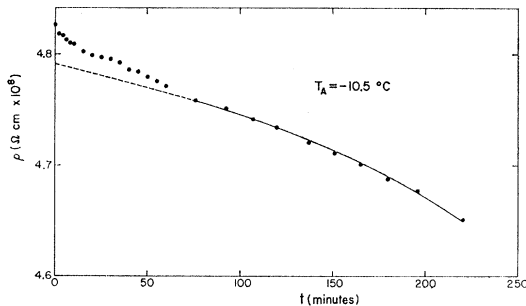


FIG. 2. The initial decrease in resistivity of a Au wire quenched from  $1000^\circ\text{C}$  in a salt bath at  $-35^\circ\text{C}$  and subsequently annealed at  $-10.5^\circ\text{C}$ .

<sup>10</sup> R. M. J. Cotterill, *Phil. Mag.* **6**, 1351 (1961).

<sup>11</sup> H. Fujiwara, Technical Report, University of Illinois, 1960 (unpublished).

sequently annealed at  $-3^\circ\text{C}$ . A much smaller effect was found now [ $\Delta\rho_0/\rho_0 = (1.3 \pm 0.1) \times 10^{-3}$  for  $\rho_0 = 5.0 \times 10^{-8} \Omega\text{cm}$ ], but the time constant was not changed. 2) After quenching at  $-35^\circ\text{C}$  a wire was annealed for 25 min at  $-3^\circ\text{C}$ , during which equilibrium should have been established. Then the specimen was pulse-heated for a few milliseconds at about  $150^\circ\text{C}$  breaking up most of the divacancies. During a subsequent anneal, again at  $-3^\circ\text{C}$ , the initial drop in resistivity reappeared with about the same values for  $\Delta\rho$  and the time constant as measured during the first anneal. These results are consistent with the view that the effect under consideration is due to the formation of divacancies.

## V. DISCUSSION

In the theoretical introduction, we considered the diffusion process involving vacancies which spent part of their life as singles and the remainder as divacancies. An expression (3) for the effective diffusion constant  $D$ , describing the flow of singles and divacancies towards sinks, was derived in terms of their diffusion constant,  $D_1$  and  $D_2$ . Furthermore, the energy of migration  $E_m$ , generally obtained from the ratio of the rates of annealing at two temperatures, was correlated with the temperature dependence of this effective diffusion constant (8). It was shown that  $E_m$  is not a simple activation energy but is temperature and concentration dependent. Knowing, however, this dependence and the energy of migration of a single vacancy  $E_m^1$ , one can determine  $E_m^2-B_2$  from (3) and (8), or more directly  $E_m^1+B_2-E_m^2$ .

First, let us evaluate  $E_m^1+B_2-E_m^2$ . Figure 3 gives the experimental data for  $E_m$  as a function of the resistivity for a gold wire quenched from  $900^\circ\text{C}$  and annealed at 30 and  $40^\circ\text{C}$  (from Fig. 1). The full curves represent the calculated energies of migration for 4 different values of  $E_m^1+B_2-E_m^2$ . Here, it is assumed that  $E_m^1=0.82$  eV, and that the concentration of vacancies is given by  $c = \rho/\rho_v$ , where  $\rho_v$  is the resistivity of 1 mole of vacancies with  $\rho_v = 1.5 \times 10^{-4} \Omega\text{cm}$ .<sup>12</sup> We see that the concept of the effective diffusion constant fits with these data for  $E_m^1+B_2-E_m^2 = 0.265 \pm 0.015$  eV.

In this run, besides single vacancies and divacancies, also higher complexes were present. Although it is shown that these higher clusters will not contribute to the diffusivity, we nevertheless had to correct for the remaining resistivity,  $\rho_r(\infty)$ , before evaluating  $E_m$ .

Palmer's experiment (Sec. IV B), on the other hand, was just arranged such as to avoid clustering, so that here no corrections have to be made. Analysis of his data gives:  $E_m^1+B_2-E_m^2 = 0.26 \pm 0.010$  eV. This is in excellent agreement with the preceding result. Taking into account the uncertainty in  $E_m^1(0.82 \pm 0.03$  eV) raises the margin for  $E_m^1+B_2-E_m^2$  to  $\pm 0.03$  eV.

Also Schottky<sup>13</sup> considered the concept of the effective

<sup>12</sup> R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **125**, 862 (1962).

<sup>13</sup> G. Schottky, *Z. Physik* **159**, 584 (1960); **160**, 16 (1960).

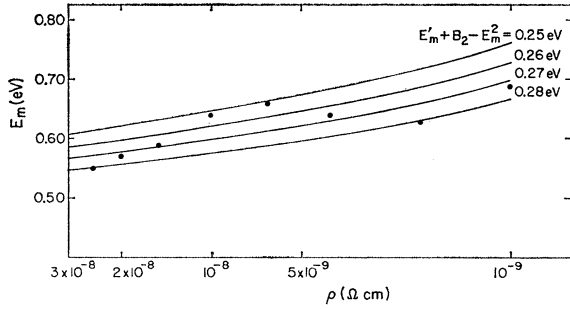


FIG. 3. The energy of migration  $E_m$  as a function of the concentration of quenched-in vacancies. The full lines are calculated by means of the Eqs. (3) and (8) for  $E_m^1 + B_2 - E_m^2 = 0.25, 0.26, 0.27,$  and  $0.28$  eV. The points correspond with the values arrived at from Fig. 1.

diffusion coefficient. Using Bauerle's published results he arrived at a value of  $\leq 0.30$  eV. The actual data, however, were not at his disposal.

$E_m^1 + B_2 - E_m^2$  can also be evaluated from a quite different experiment, namely, from the critical concentration of vacancies for which clustering will just occur. Trivacancies and higher clusters will be formed if a divacancy lives long enough to encounter a single before breaking up. This condition is expressed by Eq. (9), but now the right-hand side has to be  $\geq 1$ . It is clear from (9) that knowing the critical concentration of vacancies for given temperature one obtains directly  $E_m^1 + B_2 - E_m^2$ .

A sensitive test for the presence of clusters is the resistivity at infinite annealing times  $\rho_r(\infty)$ . Figure 4 gives  $\rho_r(\infty)$  as a function of the initially quenched-in resistivity  $\rho_0$  for all runs carried out so far at  $40^\circ\text{C}$ . Extrapolating to  $\rho_r(\infty) = 0$  shows that no clustering is to be expected for  $\rho_0 \leq 10^{-8}$   $\Omega\text{cm}$ , i.e., for  $c_1 \leq 6.7 \times 10^{-5}$ .

The critical vacancy concentration can also be derived from the resistivity for which the shape of the annealing curve changes from essentially exponential to an S shape. Koehler, *et al.*<sup>2</sup> suggested that the S-shape annealing curve is related to the formation of clusters acting as new sinks. From Bauerle's data, a  $800^\circ\text{C}$  quench seems to represent the limiting case. For this particular run  $\rho_0 = 1.5 \times 10^{-8}$   $\Omega\text{cm}$  and  $\rho_r(\infty)/\rho_0 = 0.03$ . So, combining both results,  $\rho_0 = 10^{-8}$   $\Omega\text{cm}$ , i.e.,  $c_1 = 6.7 \times 10^{-5}$  seems to be a fair estimate for the critical concentration of vacancies. Substituting in (9) gives  $E_m^1 + B_2 - E_m^2 = 0.265$  eV. We may note that in this last method,  $E_m^1 + B_2 - E_m^2$  does not depend on the choice of  $E_m^1$ , as it did in the preceding one. Earlier, Koehler *et al.*,<sup>2</sup> using the same kind of reasoning, arrived at a value of 0.275 eV.

Summarizing the results, it follows that

$$E_m^1 + B_2 - E_m^2 = 0.26 \pm 0.03 \text{ eV}$$

seems to be the best value.

A great many additional experimental values of  $E_m$  have been reported by other workers. Their results are

collected in Table II. The last column gives the energy of migration  $E_m$  as calculated from Eqs. (3) and (8). Here, we used  $E_m^1 = 0.82$  eV,  $E_m^1 + B_2 - E_m^2 = 0.26$  eV and assumed that the resistivity of 1 mole of vacancies in gold is  $1.5 \times 10^{-4}$   $\Omega\text{cm}$ .<sup>12</sup> In all cases, the calculated values agree with the experimental data within the claimed uncertainties. The data of Schule *et al.*<sup>14</sup> are too brief to allow for comparison. For a  $700^\circ\text{C}$  quench, his value of the energy of motion seems to agree with that of the other authors; a value of  $\leq 0.60$  eV for quenches from  $1000^\circ\text{C}$  is also consistent if one relates this to  $E_m^2 - B_2$  instead of  $E_m^2$  as he reports. It remains puzzling that he either finds 0.83 or 0.60 eV but no continuous range of activation energies as found by the investigators cited in Table II.

The influence of divacancies on  $E_m$  is remarkable. Even for a quenched-in resistivity of  $10^{-9}$   $\Omega\text{cm}$ , which is the smallest value for which  $E_m$  has been determined, the few divacancies present still lower the effective energy of migration  $E_m$  with respect of that for single vacancies:  $E_m^1 - E_m = 0.04 \pm 0.03$  eV. This is due to the fact that although only a few divacancies are present ( $2c_2/c_1 \sim 1.5\%$  for  $B_2 \sim 0.1$  eV), their jump frequency is about 300 times larger than that of the singles ( $E_m^2 \sim 0.66$  eV;  $E_m^1 = 0.82$  eV).

## VI. THE BINDING ENERGY OF A DIVACANCY

The above analysis of the effective energy of migration  $E_m$  gives only little information about the separate values of  $B_2$  and  $E_m^2$ . It allows us to put an upper limit on  $B_2$  and a lower limit on  $E_m^2$  ( $B_2 \leq 0.26$  eV and  $E_m^2 \geq 0.56$  eV). But if one assumes  $B_2 = 0.26$  eV, as many workers tend to believe,<sup>5,14,15</sup> one finds, consequently,  $E_m^2 = E_m^1$ . On the other hand, if  $B_2$  is very small,  $E_m^2$  will approach 0.56 eV. Meshii, Mori and Kauffman,<sup>5</sup> e.g., solved the differential equations governing the formation of di- and tri-vacancies and concluded that clustering is very likely even for quenches from below  $500^\circ\text{C}$ . Their conclusion, however, depends on the choice of their parameters. They substituted  $E_m^1 = 0.80$  eV,

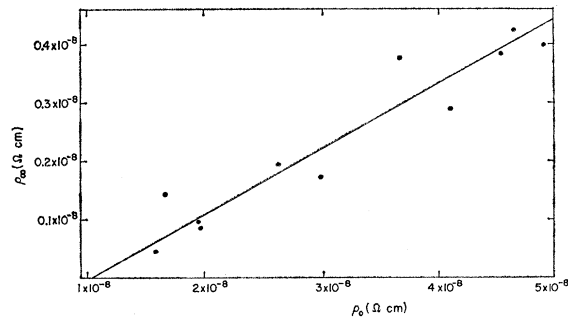


FIG. 4. The resistivity after infinite annealing time at  $40^\circ\text{C}$ ,  $\rho(\infty)$ , as a function of the initially quenched-in resistivity  $\rho_0$ .

<sup>14</sup> W. Schüle, A. Seeger, F. Ramsteiner, D. S. Schumacher, and K. King, *Z. Naturforsch.* **16a**, 323 (1961).

<sup>15</sup> H. G. van Bueren, *Imperfections in Crystals* (North-Holland Publishing Company, Amsterdam, 1961).

TABLE II. Comparison of  $E_m$  as measured by several investigators, with the calculated values of  $E_m$ .

	$T_0$ (°C)	$\rho$ at point of temperature change ( $\Omega$ cm)	$T$ anneal (°C)	$E_m$ (eV) measured	$E_m$ (eV) calculated	
Bauerle <sup>a</sup>	700	$10^{-9}$	40 and 60	$0.82 \pm 0.05$	0.78	
	800 <sup>b</sup>	$6.6 \times 10^{-9}$ – $3.5 \times 10^{-9}$	30 and 40	$0.65$ – $0.67$	$0.65$ – $0.665$	
	1000	$2.7 \times 10^{-8}$ – $1.55 \times 10^{-8}$	30 and 40	$0.55$ – $0.61$	$0.56$ – $0.59$	
Bradshaw and Pearson <sup>c</sup>	960	$1.7 \times 10^{-8}$	70 and 130	$0.68 \pm 0.05$	0.67	
	Emrick <sup>d</sup>	708	$3 \times 10^{-9}$	40 and 60	$0.82 \pm 0.09$	0.74
		723	$3 \times 10^{-9}$	40 and 60	$0.72 \pm 0.10$	0.74
Seeger <i>et al.</i> <sup>e</sup>	718	$2 \times 10^{-9}$	40 and 60	$0.82 \pm 0.05$	0.76	
	700	?	?	$0.83 \pm ?$	?	
	1000	?	?	$< 0.60$	?	
$c_1$						
DeSorbo <sup>f</sup>	820	$3.3 \times 10^{-5}$	56.1 and 62.2	0.73	0.71	
	890	$6.2 \times 10^{-5}$	50.5 and 63.9	0.64	0.67	
	920	$7.6 \times 10^{-5}$	45.9 and 48.0	0.62	0.61	

<sup>a</sup> See reference 1.

<sup>b</sup> Data corrected for the remaining resistivity  $\rho_r(\infty)$  and re-analyzed by the improved method discussed under Sec. IIIA.

<sup>c</sup> See reference 25.

<sup>d</sup> See reference 24.

<sup>e</sup> See reference 14.

<sup>f</sup> See reference 26.

$E_m^2 = 0.70$  eV, and  $B_2 = 0.3$  eV, so that  $E_m^1 + B_2 - E_m^2 = 0.4$  eV which far exceeds any reasonable upper limit.<sup>16</sup>

A more direct measure of the binding energy of a divacancy  $B_2$  can be obtained from a study of the transient process during which single vacancies and divacancies come into equilibrium with each other. The differential equations which govern this process can be defined from (1a) and (1b), and are<sup>17</sup>:

$$\begin{aligned} dc_1/dt &= -2\alpha_1 c_1^2 + 2\alpha_2 c_2, \\ dc_2/dt &= +\alpha_1 c_1^2 - \alpha_2 c_2, \end{aligned} \quad (11)$$

with the boundary conditions:

$$\begin{aligned} c_1 + 2c_2 &= c_0 \quad \text{for all } t, \\ c_2 &= 0 \quad \text{at } t=0. \end{aligned}$$

The second boundary condition is not strictly correct. By quenching from 1000°C into a bath of  $-35^\circ\text{C}$  at a speed of  $7 \times 10^5$  °C/sec, as in our experiment, the initial concentration of divacancies will correspond with the equilibrium amount present at about 350°C.<sup>11</sup> Below this temperature, namely, single vacancies and divacancies reach equilibrium at a lower rate than the quenching speed. Assuming  $B_2 = 0.1$  eV, the concentration of divacancies at 350°C is about 12 times smaller than at our annealing temperature of  $-3^\circ\text{C}$ , thus justifying the given boundary condition.

The solution of the differential Eq. (11) is

$$\frac{\Delta\rho}{\Delta\rho_0} = \frac{\coth(t_0/\tau) - \coth[(t+t_0)/\tau]}{\coth(t_0/\tau) - 1}, \quad (12a)$$

<sup>16</sup> Substituting this large value in Eq. (9) gives a critical concentration of vacancies for clustering:  $c_1 \sim 3 \times 10^{-7}$ , i.e.,  $\rho = 5 \times 10^{-11}$   $\Omega\text{cm}$ , which corresponds to a quench from 450°C.

<sup>17</sup> The time constant of this process is so small in comparison with the characteristic times for annealing of defects to sinks that the latter process is neglected.

with  $\Delta\rho/\Delta\rho_0 = c_2/c_2^e$ . Here,  $c_2^e$  is the equilibrium concentration of divacancies at the annealing temperature.  $\tau$  is the characteristic decay time of the process which is given by

$$1/\tau = 7\nu_1 e^{-(E_m^1 + B_2)/kT} (1 + 48c_0 e^{B_2/kT})^{1/2}. \quad (12b)$$

It is the time required to form 88% of the final concentration of divacancies;  $t_0$  is the integration constant to be found by substituting the boundary conditions. Finally, the total relative drop in resistivity can be expressed in terms of  $c_2^e$  by

$$\Delta\rho_0/\rho_0 = (2c_2^e/c_0)[1 - (\rho_{2v}/2\rho_v)], \quad (12c)$$

where  $\rho_v$  and  $\rho_{2v}$  are the resistivities of 1 mole of single vacancies and divacancies, respectively.

From our experiments,  $B_2$  can now be evaluated in several different ways. We will use throughout the calculation  $\rho_v = 1.5 \times 10^{-4}$   $\Omega\text{cm}$  and  $E_m^1 = 0.82 \pm 0.03$  eV.

(1).  $B_2$  can be found from the ratio of the time constants at two different annealing temperatures. In this way, the frequency factor in (12b) cancels out. Substituting  $\tau = 18$  min at  $-3^\circ\text{C}$  and 55 min at  $-10.5^\circ\text{C}$  (Sec. IV C) gives  $B_2 = 0.11 \pm 0.04$  eV.

(2).  $B_2$  can be found from the absolute values of  $\tau$ . In Eq. (12b) only the frequency factor is not very well known but its influence on the exponent is weak. Using  $\nu_1(0.6 \pm 0.4) \times 10^{13}$   $\text{sec}^{-1}$  one finds from the decay times at the two annealing temperatures:  $B_2 = 0.09 \pm 0.04$  eV and  $B_2 = 0.08 \pm 0.04$  eV, respectively. In the calculations under (1) and (2) the assigned uncertainties are obtained from the probable errors in  $\tau$  and  $E_m^1$ .

(3).  $B_2$  can also be determined from the ratio of the total relative drop in resistivity  $\Delta\rho_0/\rho_0$  at two different annealing temperatures. In Eq. (12c),  $c_2^e$  can be expressed in terms of  $B_2$  and  $c_0$  and  $c_2^e$  can be eliminated using Eq. (5) and the first boundary condition. Further-

TABLE III. The binding energy of divacancies in gold.

Method	$B_2$ (eV)
$\tau$ ratio	$0.11 \pm 0.04$
$\tau$ absolute	$0.09 \pm 0.04$
Ratio $\Delta\rho_0/\rho_0$	$0.08 \pm 0.04$
Ratio $\Delta\rho_0/\rho_0$ with preanneal	$0.10 \pm 0.02$
Average	$0.10 \pm 0.03$

more, taking the ratio of  $\Delta\rho_0/\rho_0$  at two different temperatures cancels the unknown factor in the brackets of (12c). Substituting the values for  $\Delta\rho_0/\rho_0$  and  $\rho_0$  as found by quenching from 1000°C and annealing at  $-3^\circ\text{C}$  and  $-10.5^\circ\text{C}$ , (Sec. IV C) gives  $B_2=0.10 \pm 0.02$  eV.

(4). One run was performed in which a freshly quenched specimen was pre-annealed at  $+18^\circ\text{C}$  for 5 min before cooling down to  $-3^\circ\text{C}$ . Comparing the total drop in resistivity in this case  $(\Delta\rho_0/\rho_0)_2$ , with the drop found by a direct annealing at  $-3^\circ\text{C}$ ,  $(\Delta\rho_0/\rho_0)_1$ , gives us again  $B_2$ . For this case, one can easily derive from (12c)

$$(\Delta\rho_0/\rho_0)_1 = (\Delta\rho_0/\rho_0)_2 [1 - e^{B_2(T_2 - T_1)/kT_1T_2}], \quad (12d)$$

where  $T_1$  and  $T_2$  are the pre-annealing and final annealing temperatures, respectively. It is assumed here that during the 5-min pre-anneal at  $+18^\circ\text{C}$  equilibrium between the singles and divacancies has been established. Substituting the numbers given in Sec. IV C results in:  $B_2=0.13 \pm 0.03$  eV. We may note that the methods used under (3) and (4) do not involve a numerical substitution of  $E_m^1$  as under (1) and (2), thus reducing the probable error in  $B_2$ .

Table III gives a compilation of the different results. We may note the surprising consistency between the three values obtained from an analysis of  $\tau$  and the latter two from the magnitude of the effect. The final average value can be set at  $B_2=0.10 \pm 0.03$  eV. The assigned uncertainty is much larger than one calculates from the table. It corresponds, however, more closely to the faith we feel can be put into these data, which, in fact, involves a rather small effect.

Combining the result of Sec. V with the value of the binding energy  $B_2$  derived here, gives directly the energy of migration of a divacancy  $E_m^2=0.66 \pm 0.06$  eV.

So far we have analyzed the initial drop in resistivity for the case where only single vacancies and divacancies are involved. However, as will be shown in the next section, one cannot exclude the possibility that trivacancies also will contribute in the transient process. An analysis including trivacancies (see Sec. VII) leads to  $B_2=0.07 \pm 0.03$  eV, which is within the assigned uncertainty of the previous analysis.

Although no other direct measurements of  $B_2$  are available, its very low value was suggested previously by Koehler *et al.*,<sup>2</sup> Fujiwira,<sup>11</sup> and Schottky,<sup>13</sup> all mainly based on analyses of Bauerle's data. Meshii, *et al.*<sup>18</sup>

<sup>18</sup> M. Meshii, T. Mori, and J. W. Kauffman, *Acta Met.* **9**, 71 (1961).

concluded from quench-hardening experiments that  $B_2 \sim 0.3$  eV. They found a continuous increase in yield stress on aging even for a quenched in resistivity of  $\rho_0=4 \times 10^{-9}$   $\Omega\text{cm}$  ( $T_Q \sim 700^\circ\text{C}$ ) and ascribed this effect to the formation of clusters. Apparently, however, they did not realize that clustering is not determined by  $B_2$  but by  $E_m^1+B_2-E_m^2$  [Eq. (9)]. Inserting their numbers into (9) gives  $E_m^1+B_2-E_m^2=0.28$  eV which is within the uncertainty of our estimate.

Theoretical calculations would not lead one to expect the very low divacancy binding energy in gold. Most calculations have been carried through for copper and the results of various authors differ widely.<sup>19-22</sup> Seeger and Bross<sup>20</sup> give  $B_2=0.3$  eV for all three noble metals, while March and Corless<sup>21</sup> pointed out that some of the terms neglected in their calculation may be so large as to change the sign of the interaction. Kimura, *et al.*<sup>22</sup> postulated an attractive energy of 0.4 eV for vacancies two atomic distances apart, and a repulsive one at shorter distances. In fact, this complicated picture is postulated *a posteriori* to match their model for high-temperature quenches with Bauerle's data (see II).

The only other metal for which the divacancy binding energy is measured is silver.<sup>9</sup> Here a much higher value was found:  $B_2=0.38 \pm 0.05$  eV. The large difference in binding energy for the two noble metals is still a theoretical puzzle.

Finally, knowing  $B_2$ , we can estimate the difference in resistivity of a divacancy  $\rho_{2v}$  and two separate single vacancies  $2\rho_v$  by substitution of the appropriate numbers in (12c). One finds then

$$(2\rho_v - \rho_{2v})/2\rho_v = (4.6 \pm 3) \times 10^{-2}.$$

In line with our expectation, the difference in resistivity is extremely small. This was predicted on theoretical grounds by Flynn.<sup>23</sup> He showed that the resistivities are closely related to the volumetric contractions around the defect and it appears likely that in first approximation these contractions are not very different for singles and divacancies.

## VII. THE BINDING ENERGY OF A TRIVACANCY

So far trivacancies have been neglected. In the present section, we shall investigate to what extent their introduction affects our interpretation of  $E_m$  and the analysis of the data from which  $B_2$  was derived. It will be shown in paper II, that the trivacancies in Au will be in thermal equilibrium with singles and divacancies, if their binding energy  $B_3 \leq 0.55$  eV. ( $B_3$  is the difference in energy between a trivacancy and that of a well separated single vacancy and a divacancy.) We shall see below that  $B_3 \leq 0.3$  eV.

<sup>19</sup> J. H. Bartlett and G. Dienes, *Phys. Rev.* **89**, 848 (1953).

<sup>20</sup> A. Seeger and H. Bross, *Z. Physik* **145**, 161 (1956).

<sup>21</sup> N. H. March and G. K. Corless, *Phil. Mag.* **6**, 1285 (1961).

<sup>22</sup> H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, *Acta Met.* **7**, 145 (1959).

<sup>23</sup> C. P. Flynn, *Phys. Rev.* **126**, 533 (1962).



TABLE IV. Fraction of defects combined into trivacancies at 40°C for various values of  $B_3$  and  $B_3^d$  and quenches from 900°C and 1000°C.

	$B_3=0.1$ eV	0.2 eV	0.3 eV	0.4 eV	
900°C	$2 \times 10^{-3}$	$7 \times 10^{-2}$	0.51	0.82	$B_3=B_3^d$
$c_0=10^{-4}$	$4.3 \times 10^{-4}$	$1.73 \times 10^{-2}$	0.30	0.71	$B_3-B_3^d=0.1$ eV
	$3.9 \times 10^{-4}$	$1.5 \times 10^{-2}$	0.25	0.67	$B_3-B_3^d=0.2$ eV
1000°C	$1.7 \times 10^{-2}$	0.28	0.73	0.91	$B_3=B_3^d$
$c_0=3 \times 10^{-4}$	$3.9 \times 10^{-3}$	0.11	0.59	0.82	$B_3-B_3^d=0.1$ eV
	$3.5 \times 10^{-3}$	$9 \times 10^{-2}$	0.53	0.78	$B_3-B_3^d=0.2$ eV

Let us assume that the trivacancies are in thermal equilibrium in the vicinity of room temperature. Schottky<sup>13</sup> emphasized that besides the closed packed trivacancy in the [111] plane (denoted by  $t^{60}$ , concentration  $c_3$ , and binding energy  $B_3$ ), less compact configurations also exist (to be nicknamed doglegs, denoted by  $t^d$ , concentration  $c_3^d$ , and binding energy  $B_3^d$ ), for which we may refer to Fig. 5 of Paper II. The ratio of trivacancy concentration  $3(c_3+c_3^d)$  to the total quenched-in void concentration  $c_0$ , for equilibrium at 40°C is given in Table IV for quenches from 900°C and 1000°C ( $c_0=10^{-4}$  and  $3 \times 10^{-4}$ , respectively), and for various combinations of  $B_3$  and  $B_3^d$ . Use was made of the equations for the equilibrium concentrations:

$$\begin{aligned} c_3 &= 8c_1^3 e^{(B_3+B_2)/kT}, \\ c_3^d &= 36c_1^3 e^{(B_3^d+B_2)/kT}. \end{aligned} \quad (13)$$

Here, the pre-exponential factors correspond with the number of distinguishable orientations of the trivacancy in the f.c.c. lattice. In Table IV the closed-packed triangular form  $t^{60}$  was assumed to be the most stable arrangement, i.e.,  $B_3^d < B_3$ . Examination of this table reveals that for  $B_3 \geq 0.3$  eV, a substantial part of the defects is combined into trivacancies. Examination per column shows that for  $B_3 - B_3^d \geq 0.1$  eV the contribution of doglegs is negligibly small. This can also be seen from Eq. (13) which can be written as  $c_3/c_3^d = (2/9)e^{(B_3-B_3^d)/kT}$ , the ratio is 9.1 for  $B_3 - B_3^d = 0.1$  eV.

The influence of the trivacancies on the interpretation of  $E_m$  is twofold:

(1) In the Eqs. (2) and (3) for the effective diffusion coefficient, a term has to be added representing the motion of trivacancies. Schottky<sup>13</sup> pointed out that the  $t^{60}$  can only move by the dissociation into a dogleg (see, also, Paper II) and that the doglegs are appreciably more mobile. For simplicity, we will only consider the diffusivity of the latter. The diffusion constant for trivacancies  $D_3^d$  is given in Table I.  $d_{30}$  is a geometrical factor of about 1/10. One can easily show that the migration of doglegs can be included into (3) by adding a term in the numerator:

$$f(\nu_3/\nu_1)c_1^2 \exp[+E_m^1 - E_m^3 + B_2 + B_3^d]/kT.$$

$E_m^3$  is the energy of migration of a dogleg, and  $f$  is a geometrical factor of about 12. Trivacancy motion can be neglected if the above added term is small in comparison with the divacancy term. Hence,  $c_1 < \frac{1}{8}e^{-B_3^d/kT}$

assuming that  $E_m^3 = E_m^2$  and  $\nu_3/\nu_1 = \frac{1}{3}$ . For  $c_1 = 10^{-4}$  (quench from 900°C) and  $T = 313^\circ\text{K}$ , one obtains for the above condition:  $B_3^d < 0.2$  eV.

(2) It affects the numerical substitution of  $c_1$  in Eq. (3). Let us suppose  $B_3 = B_3^d = 0.3$  eV. Then for a 900°C quench, 51% of the defects are present as trivacancies, accordingly reducing  $c_1$  to about half the value used before. Application of (3) and (8) to our data of  $E_m$  in Figs. 1 and 3, and assuming  $E_m^1 = 0.82$  eV, gives  $E_m^1 + B_2 - E_m^2 = 0.285 \pm 0.015$  eV, instead of the previous value  $0.265 \pm 0.015$  eV. Assuming  $B_3 = B_3^d = 0.4$  eV, increases this to  $0.295 \pm 0.02$  eV. No significant change is found for  $B_3 = B_3^d = 0.2$  eV. However,  $E_m^1 + B_2 - E_m^2 > 0.26$  eV seems to be rather unlikely because it leads to important alterations in the interpretation of  $E_m^1$  as obtained from Bauerle's<sup>1</sup> and Emrick's<sup>24</sup> data of quenches from 700°C. It was mentioned earlier that in these cases (Table II) even very low divacancy concentrations decrease the actually measured activation energy  $E_m$  with respect to  $E_m^1$  considerably. For  $E_m^1 + B_2 - E_m^2 = 0.26$  and 0.29 eV, one finds for Bauerle's data:  $E_m^1 - E_m = 0.04$  and 0.095 eV, respectively, and for Emrick's data: 0.08 and 0.17 eV. In both cases, the first values are within the author's claimed uncertainties in  $E_m^1$  (Table II). On the other hand, in order to account for the higher values in  $E_m^1 - E_m$ , one has to assume that  $E_m^1$  is about 0.90 eV. This is ruled out because one can set the value of  $E_m^1$  safely at  $E_m^1 = 0.82 \pm 0.03$  eV as the average of measurements of various investigators and by independent methods.<sup>1,12,14,24-26</sup> It thus follows that  $B_3$  is very probably less than 0.3 eV.

Summarizing the results of (1) and (2), one can conclude that a tightly bound trivacancy would produce important changes in the assignment of the motion and binding energies for simpler defects. Since independent evidence exists for the present assignments, one must conclude that  $B_3 < 0.3$  eV and  $B_3^d < 0.2$  eV. It can be seen from Table IV that this, in fact, means that the fraction of defects combined into trivacancies has to be less than 10%.

If the binding energy of a trivacancy is indeed  $< 0.3$  eV, our analysis of the data in Fig. 2 which lead to the evaluation of  $B_2$  has to be reconsidered. The time  $\tau_3$  required for the trivacancies to achieve equilibrium with singles and divacancies is given by  $\tau_3 = 1/\gamma_2$  (see, also, Paper II). For  $B_3^d < 0.3$  eV,  $\tau_3$  becomes comparable with the decay time of the transient process involving only singles and divacancies. One can, therefore, not exclude the possibility that one deals in this experiment with the transient process involving singles, di-, and trivacancies. We have not been able to integrate the three coupled differential equations describing this process [Eqs. (1a), (1b), and (1c)]. Instead, we solved them numerically, assuming that the resistivity of a divacancy

<sup>24</sup> R. Emrick, Phys. Rev. **122**, 1720 (1961).

<sup>25</sup> F. J. Bradshaw and S. Pearson, Phil. Mag. **2**, 379 (1957).

<sup>26</sup> W. DeSorbo, Phys. Rev. **117**, 444 (1960).

is equal to that of two singles ( $2\rho_v^j = \rho_{2v}$ ). We found that  $B_2 = 0.07 \pm 0.03$  eV and  $B_3^d = 0.3 \pm 0.1$  eV. The binding energy of a divacancy is even somewhat smaller than before but is still within the assigned uncertainty of the previous analysis. The value of  $B_3^d$  is not inconsistent with our estimates given above.

### VIII. CONCLUSION AND SUMMARY

In summary, the best available values for the energies of formation and motion of vacancies and divacancies in gold are  $E_M^1 = 0.82 \pm 0.03$  eV,  $E_F^1 = 0.96 \pm 0.04$  eV,  $E_M^2 = 0.66 \pm 0.06$  eV,  $B_2 = 0.10 \pm 0.03$  eV,  $B_3 \leq 0.3$  eV, and  $B_3^d \leq 0.2$  eV. In addition, if only single vacancies and divacancies are present and if they are in thermal equilibrium, then the diffusion of voids can be described using an effective diffusion constant. The effective diffusion constant expresses the fact that each vacancy during its random walk spends part of its lifetime as a single vacancy and part of its lifetime as a divacancy.

In conclusion, we like to compare our results on Au with the behavior of vacancies in quenched Ag. The life history of the defects in the two noble metals is completely different, mainly because of the large difference

in binding energy for the divacancy. For Au, we measured  $B_2 \cong 0.10$  eV, for Ag, Doyama and Koehler<sup>9</sup> reported  $B_2 \sim 0.38$  eV. Therefore, in Au both singles and divacancies are present in the vicinity of room temperature. The defects anneal out by diffusing part of their lifetime as singles and the remainder as a member of a divacancy. The measured energy of migration  $E_m$  for this process is not a constant but depends on temperature and concentration of defects as observed. The minimum value of  $E_m$  is  $E_m^2 - B_2$  ( $\sim 0.55$  eV), and not the energy of migration for divacancies  $E_m^2$ . In Ag, on the other hand, the binding energy for divacancies is so large that all the quenched-in defects will be combined into pairs, and the energy of migration which one measures below room temperature is  $E_m^2$  ( $\sim 0.57$  eV).

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## Annealing of Pure Gold Quenched from above 800°C†

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The decrease of quenched-in resistivity as a function of time of Au wires quenched from above 800°C and then annealed in the vicinity of room temperature, is observed to be an *S*-shaped curve. The time  $t_{1/2}$  required for half of the initially quenched-in resistivity  $\rho_0$  to anneal out decreases from 15 to 0.5 h as quenching temperature is raised from 840 to 1000°C. It is observed that  $1/t_{1/2} \propto \rho_0^{(2.60 \pm 0.2)}$ . The fraction of  $\rho_0$  that remains after infinite annealing times is independent of the quenching temperature with  $\rho_r(\infty)/\rho_0 = 0.074 \pm 0.006$ . All the *S*-shape annealing data combine into one universal curve if  $f = [\rho - \rho_r(\infty)] / [\rho_0 - \rho_r(\infty)]$  is plotted against the reduced time  $t/t_{1/2}$ . The universality of the curves indicates that the supersaturated concentrations of defects in Au disappear by one unique process. The following process is proposed: The defects in freshly quenched specimens are present as single vacancies, divacancies, and trivacancies, which are in thermal equilibrium with one another. The concentration of other

complexes is negligible. Tetrahedra of stacking faults, as observed by Hirsch, act as the sinks for singles and divacancies. They are formed during annealing by the collapse of six aggregated vacancies; their nucleation sites are the tetravacancy complexes, which are the smallest vacancy clusters in Au which are not in thermal equilibrium. The tetravacancy converts into a tetrahedron if struck by a divacancy. The remaining resistivity is due to the stacking faults of the tetrahedra. If it is assumed, in addition, that all the quenched-in defects disappear at the tetrahedra, then  $\rho_r(\infty)/\rho_0$  is shown to be a constant as observed and the parameter  $f$  then represents the fraction of the initially quenched-in defects that has not yet been absorbed. The model predicts that  $1/t_{1/2} \propto c_0^{2.5}$  and that the number of tetrahedron  $n_\infty$  at infinite annealing times is  $n_\infty \propto c_0^{1.5}$  in agreement with the experiments. The resistivity of stacking faults per unit area was calculated to be  $(1.3 \pm 0.4) \times 10^{-13}$   $\Omega\text{cm}^2$ .

### I. INTRODUCTION

IT was observed by Bauerle and Koehler<sup>1</sup> that if Au wires are quenched from above 800°C and subsequently annealed in the vicinity of room temperature,

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<sup>1</sup> J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).

the annealing curve is not essentially exponential, but has an *S* shape (Fig. 1). The time required for half of the resistance increment to anneal decreases as the quenching temperature is raised. In addition, about 7% of the quenched-in resistivity cannot be annealed out in the neighborhood of room temperature.

The data for quenches from various high temperatures can all be plotted on one graph if  $f$ , the fraction