

Interpretation of the Quenching Experiments on Gold*

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The behavior of vacancies in gold during quenching is treated theoretically under the assumption that the total number is conserved, although they may aggregate into pairs and triplets. Approximate solutions of the equations governing the abundance of isolated vacancies is obtained in the case in which only a small fraction aggregate, that is, in the limit in which the quench is very rapid. This situation appears to correspond to that observed in gold when the rate of quench is near 3×10^4 degrees per sec. It is concluded that the binding energy of a pair of vacancies is between 0.1 and 0.2 ev and that the activation energy for migration of a pair is lower than that of a single vacancy by no more than 0.2 ev.

I. INTRODUCTION

THE quenching experiments described in the preceding paper are important because one of the defects retained presumably is responsible for self-diffusion in pure gold. The experiments were actively pursued initially to obtain information concerning this defect. However, careful annealing measurements near room temperature revealed an unsuspected complexity in behavior. Fortunately, as will be seen, this additional wealth of information enables new conclusions to be drawn about the nature of the defects involved.

In an effort to understand in detail what takes place, we would like to follow the defects concerned from their birth in the circumstances governing thermal equilibrium at the high quenching temperature, through the quenching process, to their disappearance during a room-temperature anneal.

Before discussing the life history of the defects which are quenched in, it is necessary to consider the relative abundances of vacancies and interstitial atoms. Huntington and Seitz^{1,2} and Huntington³ have made calculations which give estimates of the energy required to form a lattice vacancy and an interstitial copper atom in copper. They found that the energy of formation of an interstitial probably is about 4.5 ev, whereas that of a vacancy is near 1.2 ev. Thus, the equilibrium ratio of interstitial to vacancy concentration at 800°C would be about 10^{-15} if these estimates are approximately correct. Since the values of the formation energies are not expected to differ much in gold and copper, interstitials are not believed to be important in the experiments to be described here. We shall assume the defects quenched are vacancies in either single or aggregated form.

The differential equations which govern the concentrations of defects are:

$$\frac{\partial c}{\partial t} = -16c^2\nu \exp(-E_M^v/kT) + 2c_2\nu_2' \exp[-(E_M^v+B)/kT] + D \left\{ \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right\} - 24\nu_2 c c_2 \exp(-E_M^2/kT) + c_3\nu_3' \exp[-(E_M^2+\Delta)/kT], \quad (1)$$

$$\frac{\partial c_2}{\partial t} = +8c^2\nu \exp(-E_M^v/kT) - c_2\nu_2' \exp[-(E_M^v+B)/kT] + D_2 \left\{ \frac{\partial^2 c_2}{\partial r^2} + \frac{1}{r} \frac{\partial c_2}{\partial r} \right\} - 24c c_2 \nu_2 \exp(-E_M^2/kT) + c_3\nu_3 \exp[-(E_M^2+\Delta)/kT], \quad (2)$$

$$\frac{\partial c_3}{\partial t} = +24c c_2 \nu_2 \exp(-E_M^2/kT) - c_3\nu_3' \exp[-(E_M^2+\Delta)/kT]. \quad (3)$$

Here c , c_2 , c_3 are the fractional vacancy, divacancy, and trivacancy concentrations; ν and ν_2 are the appropriate frequency coefficients for migration of a vacancy and a divacancy whereas ν_2' and ν_3' are the corresponding coefficients for dissociation of a divacancy and a trivacancy. We shall set $\nu_2' = \nu_2$. E_M^v and E_M^2 are the energies of motion of a vacancy and a divacancy, respectively; B is the decrease in the energy of the crystal when two well-separated vacancies combine to form a divacancy; Δ is the decrease in energy when

a vacancy and a divacancy combine to form a trivacancy; r is the distance between a vacancy or a divacancy and the axis of a dislocation; D is the diffusion constant for lattice vacancies, i.e., $D = \nu a^2/6 \exp(-E_M^v/kT)$, where a is the smallest interatomic distance. Similarly $D_2 = (1/24)\nu_2 a^2 \exp(-E_M^2/kT)$. We have neglected the fact that there is an energy of interaction between a lattice vacancy and a dislocation which can increase the rate at which vacan-

¹ H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942).

² H. B. Huntington, Phys. Rev. **61**, 325 (1942).

³ H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

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cies arrive at dislocations. The total elastic binding energy of a vacancy to a complete dislocation in copper is about a tenth of an electron volt.⁴ Thus, there is every reason to believe that the force aiding annealing at dislocations is negligible if the vacancy is more than a few atomic distances from the dislocation.

In the first equation, the first term on the right describes the loss of vacancies by formation of divacancies. The second term gives the rate of production of vacancies by dissociation of divacancies. The third term describes the loss of vacancies at dislocation sinks. The boundary conditions both at the dislocations and midway between dislocations are important. It is assumed here that the concentration changes which occur in the vicinity of the dislocation take place sufficiently slowly that the vacancy concentration is maintained at the equilibrium value for the temperature in question at all points along the dislocation. This assumption presupposes that the diffusion of vacancies along the dislocation from the jogs is much more rapid than the diffusion of vacancies in a direction normal to the dislocation axis.⁵ Hence, the appropriate boundary condition at the dislocation is:

$$c = \exp(-E_F^v/kT) \text{ at } r=b, \text{ all } t, \quad (4)$$

where E_F^v is the energy required to form a lattice vacancy and b is two or three times a . If $2R$ is the distance between dislocations:

$$\partial c/\partial r=0, \quad (r=R, \text{ all } t). \quad (5)$$

Similar boundary conditions hold for divacancies. Since trivacancies probably are mobile there should be a term describing their motion. It is difficult to estimate its importance.

These equations are very general. They should give the equilibrium concentrations of defects; they should also describe the concentration changes which occur during quenching and annealing.

II. EQUILIBRIUM CONCENTRATIONS

Consider first the equilibrium concentrations. Assume here that the quenched-in resistivity measures the vacancy concentration in equilibrium at the quenching temperature (i.e., the temperature from which the sample is quenched). Experimentally, quenched-in resistivity varies with the quenching temperature as follows:

$$\Delta\rho = A \exp(-E_F^v/kT).$$

The value of A found for gold is 4.89×10^{-4} ohm cm. It was also found during annealing that the decreases in resistivity were accompanied by decreases in length. If

⁴ A. Seeger, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7, p. 557; J. Friedel, *Dislocations* (Gauthier-Villars, Paris, 1956), p. 237 obtains a larger interaction energy in copper, i.e., 0.35 ev by noting that a vacancy can allow a local relaxation of the dislocation stresses.

⁵ D. Turnbull, *Bristol Conference on Defects in Solids* (Physical Society, London, 1955), p. 203.

one supposes that the dimensional changes are isotropic, the resistivity and the fractional change of volume $\Delta v/v$ are related by the equation $K\Delta v/v = \Delta\rho$. Experimentally, $K = 3.2 \times 10^{-4}$ ohm cm for gold. If the volume of the crystal increases by one atomic volume when a lattice vacancy is produced, $c = \Delta v/v = 1.53 \exp(-E_F^v/kT)$. On the other hand, if there is some relaxation around a vacancy so that the increase in volume per vacancy is 0.4 times the atomic volume,⁶ the coefficient in front of the exponential is 3.82. The relatively small values of the coefficient in these two areas indicate the alterations in the atomic vibrational frequencies near a vacancy do not appear to contribute materially to the pre-exponential factor.⁷ Using the experimental values of K and the two estimates of the volume increase per vacancy, we find that the resistivity increase for 1 atomic percent vacancies is 3.2×10^{-6} and 1.3×10^{-6} ohm cm, respectively. It is interesting to note that the "best" of the theoretical calculations of the resistivity⁸ agree with the second value and suggest that the volume increase per vacancy is close to 0.4 times the atomic volume.

Consider next the divacancy concentration which is at equilibrium at the high temperature and is present after quenching. Bartlett and Dienes⁹ estimate that B , the binding energy of a divacancy, is between 0.23 and 0.59 ev in copper, whereas Seeger and Bross¹⁰ found $B = 0.3$ ev for all three noble metals. Since the nearest-neighbor relaxation is expected to be larger near a divacancy than near a single vacancy, we shall assume that $\nu/\nu_2 = 2.25$. We may note that the first two terms on the right side of Eq. (1) must give zero under equilibrium conditions and use this fact to determine the ratio of the concentration of divacancies to that of vacancies. Table I gives vacancy concentrations and divacancy to vacancy ratios for equilibrium conditions at various high temperatures and values of B equal to 0.3 ev, 0.2 ev, and 0.1 ev which we believe is the appropriate range to consider.

We note from the table that c_2/c lies in the range between 0.14 and 0.01 for the two highest temperatures in the range of B considered. It has sometimes been

TABLE I. Equilibrium concentrations of vacancies and divacancies.

T	c	$B=0.3$ ev c_2/c	$B=0.2$ ev c_2/c	$B=0.1$ ev c_2/c
600°C	0.840×10^{-5}	8.154×10^{-3}	2.158×10^{-3}	5.712×10^{-4}
700°C	3.203×10^{-5}	2.065×10^{-2}	6.264×10^{-3}	1.900×10^{-3}
800°C	9.521×10^{-5}	4.398×10^{-2}	1.491×10^{-2}	5.056×10^{-3}
900°C	2.351×10^{-4}	8.234×10^{-2}	3.061×10^{-2}	1.138×10^{-2}
1000°C	5.034×10^{-4}	13.963×10^{-2}	5.611×10^{-2}	2.254×10^{-2}

⁶ C. W. Tucker, Jr., and J. B. Sampson, *Acta Met.* **2**, 433 (1954).

⁷ G. H. Vineyard and G. J. Dienes, *Phys. Rev.* **93**, 265 (1954).

⁸ P. Jongenberger, *Appl. Sci. Research* **B3**, 237 (1953); F. Abelès, *Compt. rend.* **237**, 796 (1953); F. J. Blatt, *Phys. Rev.* **103**, 1905 (1956); **99**, 1708 (1955).

⁹ J. H. Bartlett and G. J. Dienes, *Phys. Rev.* **89**, 848 (1953).

¹⁰ A. Seeger and H. Bross, *Z. Physik* **145**, 161 (1956).

supposed that vacancy pairs in metals diffuse much more rapidly than single vacancies. This postulate seems possible in gold only if the binding energy B of the divacancy is exceedingly small. We note, first, that Okkerse¹¹ did not observe any deviations between the results obtained at high and low temperatures in his measurements of self-diffusion coefficient in gold, which extend to 950°C. It follows that either the density of pairs is small at the higher temperatures or the diffusion coefficient of a pair is not radically different from that of a single vacancy. Combining the energy of formation of a vacancy, given above, with the observed activation energy for diffusion, namely 1.71 eV, we conclude that the energy of migration is near 0.80 eV. This leads us to a diffusion coefficient of about 0.458×10^{-6} cm²/sec at 900°C if we assume that $\nu = 10^{13}$ sec⁻¹. For comparative purposes, we shall assume somewhat arbitrarily that the energy of migration of a pair is 0.6 eV. We then obtain a diffusion coefficient of 0.366×10^{-6} cm²/sec at the same temperature, which is about 0.80 times larger than that for single vacancies. Thus, even if pairs possessed this relatively small mobility, they would produce an observable change in the self-diffusion coefficient of the metal if B were near to or larger than 0.3 eV.

In other words, we are led to conclude either that divacancies migrate in much the same way as single vacancies, or their binding energy is not larger than 0.3 eV. We shall amplify this conclusion later and conclude that B should be nearer 0.1 eV.

If divacancies were to predominate at high temperatures and be responsible for self-diffusion in gold, it would be necessary to require that $B \geq E_F^v$. If $B = E_F^v$ and if the measured energy of formation is that of divacancies, then $B = E_F^v = E_F^2 = 0.98$ eV. This is a rather large value for B .

III. CHANGES DURING QUENCHING

Consider next the behavior of vacancies during quenching. The essential features of events during a rapid quench can be obtained if one assumes that only a negligible number of vacancies and divacancies are lost by diffusion to dislocations. We shall see that this hypothesis is reasonable.

Although the total number of vacant sites remains constant during the quench, the concentration of divacancies may be expected to grow at the expense of the single vacancies. Experimentally, the temperature and time are related in the manner

$$T = T_0 - \beta t$$

during quenching. Here T_0 is the quenching temperature and β is the quenching rate. It is found that an appreciable amount of recombination and breakup occur during rapid cooling if B lies in the range from 0.1 eV to

¹¹ B. Okkerse, Phys. Rev. **103**, 1246 (1956). See also Makin Rowe, and Le Claire, Proc. Phys. Soc. (London) **B70** (June, 1957).

TABLE II. Fraction of vacancies which are single before and after quenching.

	Before	40°C	After ^a 60°C	120°C
$B = 0.1$ eV				
600°C	0.9994	0.9878	0.9902	
700°C	0.9962	0.9551	0.9637	0.9784
800°C	0.9900	0.8774	0.8994	0.9384
		0.8860 ^b		
900°C	0.9777	0.7435	0.7836	0.8604
		0.7581 ^b		
1000°C	0.9569	0.5751	0.6284	0.7422
$B = 0.2$ eV				
600°C	0.9957	0.8544 ^c	0.8544 ^c	0.9000
700°C	0.9877	0.5542 ^c	0.5542 ^c	0.7025
800°C	0.9711	0.1494	0.2151	0.4427
$B = 0.3$ eV				
600°C	0.9839		0.1816 ^c	

^a Values after quenching with no superscript are equilibrium values at the specified temperature.

^b Quenching rate 6×10^4 °C/sec.

^c Quenching rate 3×10^4 °C/sec.

0.3 eV, so that terms corresponding to both effects are important. Since the defects are in thermal equilibrium, we have the initial conditions $\partial c/\partial t = \partial c_2/\partial t = 0$. The equations are solved in the appendix under the assumption that only small changes occur during quenching. The result is

$$Z = Z_0 + \frac{32\nu Z_0^2 (E_M + B) r_0^{1-s} \exp(-E_M/kT_0)}{y_0^{2s} \left(1 + \frac{2}{y_0}\right) \beta k (tr_0)} \times \left\{1 - \frac{(tr_0)^s (1-s)!}{(1-s)}\right\}. \quad (6)$$

Here Z is the ratio of the concentration of single vacancies to that of total vacancies after quenching, Z_0 being the ratio for thermal equilibrium at the quenching temperature. It is assumed that the difference between Z and Z_0 is small. The other symbols represent the following quantities:

$$s = B/(E_M + B),$$

$$y_0 = (E_M + B)/kT_0,$$

$$t = \nu_2 (E_M + B)/\beta k,$$

$$r_0 = \frac{e^{-v_0}}{y_0^2} \left(1 - \frac{2}{y_0} + \frac{6}{y_0^2} - \frac{24}{y_0^3} + \frac{120}{y_0^4} - \dots\right).$$

The fraction of single vacancies is given in Table II before and after quenching from various temperatures. The equilibrium value of the ratio has been given for temperatures near room temperature for low values of B . In this case, the assumption is made that the total concentration of voids is conserved during quenching.

However, it is also assumed that sufficient time elapses at the low temperature to attain the equilibrium ratio of double to single vacancies. The resulting ratio is given by Eq. (6) for larger values of B and sufficiently fast quenches. This equation tends to overestimate the formation of divacancies, because the integration is carried to the absolute zero of temperature. In all cases in which (6) gives a larger number of divacancies than the equilibrium result for the temperature in question, the equilibrium value was used. In a few cases, two values, an equilibrium value and a result derived from Eq. (6), are given. The quenching rate of 3×10^4 °C/sec was sufficiently low in these cases that equilibrium could be achieved; however, the more rapid rate of 6×10^4 °C/sec was sufficiently fast that a nonequilibrium ratio was retained. Both the equilibrium ratio and that for the fast quench are given in this case. We have used $\nu = 10^{13}$ cycles per second, $E_M = 0.80$ ev, and $\nu/\nu_2 = 2.25$.

An examination of Table II indicates that B must be less than 0.3 ev. If this were not the case, the defects quenched from all the temperatures used would be divacancies and perhaps other larger vacancy clusters. In fact, Table II implies that B must be less than 0.2 ev. Otherwise, one would have essentially no single vacancies present after a quench from 800°C. As we shall see, the annealing behavior after a quench from 800°C leads one to believe that an appreciable number of single vacancies are present. Hence, B must be small if the annealing found on quenching from 600°C and 700°C is to be interpreted in terms of single vacancies. This conclusion is in agreement with the earlier discussion according to which a small value of B is required if vacancies are to predominate at equilibrium at the high temperatures. It should be noted that the defect which is present in largest concentration after a 1000°C quench is the divacancy or some larger cluster even if B is of the order of 0.15 ev.

Another conclusion can be drawn from the fact that the resistivity retained is not very dependent on the quenching rate. Table II shows that on quenching from 900° or 1000°C one has an appreciable concentration of divacancies for any of the values of B given. Suppose the energy of motion of a divacancy were as low as 0.3 ev. A simple analysis shows that in this case the divacancies, and hence a large fraction of the resistivity, would disappear within a few seconds in any specimen held at 40°C. Since the resistivity is retained easily and a large transient is not found on annealing at room temperature, one is compelled to conclude that the energy of migration of divacancies is not as low as 0.3 ev.

IV. ANNEALING AT ROOM TEMPERATURE

The annealing behavior is complex and depends upon the quenching temperature. As the quenching temperature increases, the rate of annealing observed at 40°C increases; a decrease is observed in the measured energy

of motion. Moreover, when the quenching temperature is high, not all of the quenched-in resistance anneals out at 40°C.

This behavior can be understood in a semiquantitative way by noting that one should obtain more vacancies than divacancies on quenching to room temperature from a low temperature. In contrast, more divacancies and other larger clusters are to be expected on quenching from higher temperatures. Hence, one expects the quantities measured to reflect the properties of divacancies and perhaps of larger clusters rather than of vacancies, as one raises the quenching temperature.

Experimentally, the room-temperature annealing following a quench from below 750°C obeys first-order annealing kinetics. The specimen behaves as though the vacancies were diffusing to dislocations. The differential equation describing this process is

$$\frac{\partial c}{\partial t} = D \left\{ \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right\}. \quad (7)$$

The boundary and initial conditions are

$$\begin{aligned} c &= 0 & \text{at } r &= b, & \text{all } t; \\ \partial c / \partial r &= 0 & \text{at } r &= R, & \text{all } t; \\ c &= c_0 & \text{at } t &= 0, & \text{all } r. \end{aligned} \quad (8)$$

The first boundary condition should require that the concentration at the dislocation be equal to the equilibrium concentration appropriate for room temperature. However, this concentration is so small in comparison with c_0 , the equilibrium concentration at the quenching temperature, that we select it to be zero. The solution is

$$c = c_0 \sum_{n=1} \{ A_n J_0(\alpha_n r) - B_n N_0(\alpha_n r) \} \exp(-D\alpha_n^2 t). \quad (9)$$

Here J_0 and N_0 are Bessel's functions of the first and second kinds, respectively. The first two boundary conditions are used to determine A_n and α_n , whereas the last condition is used to determine the B_n . The first two values of α are $\alpha_1 = 0.486/R$ and $\alpha_2 = 4.032/R$. Upon using the series in such a way as to include terms with $n=1$ and $n=2$, the third boundary condition was satisfied at 0.1 R and 0.6 R . In fitting the conditions at the dislocation, we have taken $b=a$. The resulting values of the constants are $A_1 = 1.176$, $B_1 = 0.1800$, $A_2 = 0.2318$, $B_2 = 0.04585$. Thus, the series converges rapidly. Note that this description of annealing agrees with the observed behavior, that is, there is an exponential decay with a small portion which falls more rapidly in the initial stage of the anneal. The time required for the concentration to decay to one ϵ th the original value is

$$t_1 = \frac{e^{+E_M/kT}}{0.2362} \left(\frac{R}{a} \right)^2. \quad (10)$$

The annealing time is inversely proportional to the dislocation density and is independent of the vacancy

concentration. There is some question concerning the value of E_M which should be used. At 700°C one finds $E_M = 0.82 \pm 0.05$ ev. If one uses the activation energy for self-diffusion measured by Okkerse¹¹ and the energy of formation of the defects, one finds $E_M = Q - E_F = 0.73$ ev. We have used $E_M = 0.80$ ev since this value appears in the annealing experiments. Bauerle observes that the time for the concentration to decay by one n th after a quench from 600°C is 72.2 hours during an anneal at 60°C. Inserting these numbers into the foregoing expression one finds that $(R/a)^2 = 0.478 \times 10^6$ if $\nu = 10^{13}$ cycles per second. Taking a to be one atomic diameter we find that about 10^6 jumps are required before a vacancy reaches a dislocation. This would imply a large dislocation density, i.e., $n = 8.9 \times 10^8$ dislocations per cm². However, there probably is a small attractive interaction between lattice vacancies and dislocations. This can be taken into account by supposing that the capture cross section of a dislocation has a radius which is several atomic diameters, i.e., that a is several atomic diameters. Thus, if a is three atomic diameters, the dislocation density is 10^8 dislocations per cm², whereas it is 10^7 if a is ten atomic diameters. It is clear, of course, that further work should be carried out to establish a correlation between the dislocation density and the annealing time in specimens quenched from low temperatures. In this connection, the influence of deformation after a low-temperature quench should be studied. Further precise measurements should be made to determine accurately the energy of motion in a specimen quenched from 600°C.

If defects anneal only at dislocations and not by recombination, the spatial distribution which exists after a quench can be found by solving Eq. (7) with boundary conditions (8). The diffusion constant in this case is not a constant but depends on time; in fact,

$$D = \nu a^2 \exp[-E_M/k(T_0 - \beta t)], \quad (11)$$

for vacancies. Here T_0 is the quenching temperature and β is the quenching rate. Inserting this into the differential equation, separating variables, and solving, one finds that the concentration at a distance r from the dislocation after quenching is given by

$$c = c_0 \sum_{n=1} \{A_n J_0(\alpha_n r) + B_n N_0(\alpha_n r)\} \times \exp\left(-\alpha_n^2 \nu a^2 \frac{E_M}{k\beta} F(z_0)\right), \quad (12)$$

where

$$F(z_0) = \frac{e^{-z_0}}{z_0^2} \left\{ 1 - \frac{2}{z_0} + \frac{6}{z_0^2} - \frac{24}{z_0^3} + \frac{120}{z_0^4} - \dots \right\},$$

$$z_0 = E_M/kT_0.$$

The constants $A_n B_n$ and α_n take the same values as

before. Using $E_M = 0.7$ ev and the values of the parameters previously given, one finds that the exponentials associated with $n=1$ and $n=2$ have the values 0.838 and 4.8×10^{-5} after an 800°C quench if $\beta = 5 \times 10^4$ °C per second. In contrast, the exponentials take the values 0.700 and 2.3×10^{-11} if $\beta = 2.5 \times 10^4$ °C per second. Moreover, the exponentials are 0.979 and 0.245 in the case of a 600°C quench if $\beta = 5 \times 10^4$ °C per second. Finally, the exponentials are 0.959 and 6.01×10^{-2} if $\beta = 2.5 \times 10^4$ °C per second and the quench is from 600°. Hence, none of the terms having n greater than one remain after quenching from 800°C, whereas one may expect a little of the fast component with $n=2$ after a salt-water quench from 600°C. Doubling the quenching rate at 800°C and at 600°C increases the amount quenched in by 19.7% and 7.1%, respectively. The experiments indicate that doubling the quenching rate increases the amount quenched in by about 15% in both cases. Thus, the theoretical results are in reasonable agreement with the experiments. Actually, the behavior is considerably more complex than this analysis would indicate. We conclude that the theory gives about the right order of magnitude for the quenching rates required to retain the defects, if defects having energies of motion in the range 0.6 to 0.8 ev disappear by diffusion to dislocations.

There is still the problem of accounting for the gradual increase in rate and the decrease in the measured energy of motion as the quenching temperature increases. We note that as the quenching temperature increases, the fraction of divacancies and larger clusters rises. For simplicity, let us discuss the matter by assuming that only vacancies and divacancies are involved. This will illustrate the principles involved. Consider a single vacancy. If τ_1 is the length of time it diffuses before encountering another vacancy, we have

$$1/\tau_1 = 8\nu e^{-E_M/kT_0}.$$

The divacancy so formed will diffuse for a time τ_2 before it disintegrates into single vacancies. For this case,

$$1/\tau_2 = \nu e^{-(E_M+B)/kT_0},$$

where we assume that the vacancies must separate by at least one atomic distance to be considered dissociated. One can, therefore, define an effective diffusion constant D_e for the vacancy-divacancy complex as follows:

$$D_e = (\tau_1 D + \tau_2 D_2) / (\tau_1 + \tau_2). \quad (13)$$

Here D is the diffusion constant for vacancies and D_2 that appropriate for divacancies (Sec. I). Qualitatively the gradual decrease in the energy of motion occurs because the defects spend a larger fraction of their lifetime as divacancies, or larger clusters, if the initial concentration of defects is high. This picture will also account for the decrease in the annealing time. A drop of E_M in Eq. (10) from 0.80 ev to 0.60 ev will

produce a drop in annealing time from 72.2 hours to 0.0678 hour on annealing at 60°C if there is no change in sink density. This is not very different from the change actually observed (t is about 0.2 hour after a quench from 1000°C).

The annealing which takes place in a simple quench from temperatures near 850°C or higher is sufficiently complex to make detailed description difficult presumably because larger clusters are present. Let us examine this matter. As the defect concentration gradually increases, one would expect larger clusters to play an important role when a divacancy has sufficient time to encounter another single vacancy and form a trivacancy before the divacancy breaks up. One can expect a trivacancy to form in time τ_3 given by the equation

$$1/\tau_3 = 24\nu_2' \exp(-E_M^2/kT)c.$$

Hence, one expects clusters to become important when

$$\tau_3 < \tau_2,$$

or when

$$1 < \tau_2/\tau_3 = 3\nu_2'/\nu c \exp[(E_M + B - E_M^2)/kT]. \quad (14)$$

After a 700°C quench we find $\tau_2/\tau_3 = 0.62$ for an anneal at 60°C. It has been assumed here that $E_M + B - E_M^2 = 0.275$ ev. Thus, we can arrange matters so that an average divacancy breaks up before it encounters another vacancy. For a quench from 800°C, annealed at 60°C, $\tau_2/\tau_3 = 1.84$ so that some clustering might be expected here. To achieve this result, it is necessary to assume that both B and $E_M - E_M^2$ are small quantities, of the order of 0.15 ev. Equation (14) predicts that it should be possible to suppress clustering by annealing at a sufficiently high temperature. For example, at 120°C, $\tau_2/\tau_3 = 0.43$ instead of 1.84. Thus, first-order annealing should be observed in a sample quenched from 800°C. The annealing time is short, being 1.53 hours, but not too short to make reasonably accurate measurements.

The annealing observed in gold specimens quenched from below 750°C implies that dislocation climb occurs. The driving force for climb is the desire of the specimen to eliminate the large supersaturation of vacancies. According to Bardeen and Herring,¹² the decrease in free energy per vacancy is

$$\mu_v = kT \log(c/c_e). \quad (15)$$

We find $\mu_v = 0.695$ ev for a specimen quenched from 800°C and held at 40°C initially, whereas a specimen quenched from 600°C and held at 40°C has an initial chemical potential per vacancy of $\mu_v = 0.630$ ev. Bardeen and Herring point out that climb is difficult in the noble metals where the dislocations have partial form and

associated stacking faults. They note that the supersaturation is equivalent to a pressure

$$p = \mu_v/\Omega_0, \quad (16)$$

where Ω_0 is the atomic volume. For gold quenched from 800°C $p = 0.92 \times 10^{11}$ dyne/cm². Thus the driving force for climb is very large, although the detailed way in which climb occurs is obscure. The experiments indicate that climb does indeed occur on annealing at 40°C after a quench from 700°C, for it is found that both the resistance and the change in length follow the same curve. If appreciable clustering occurred, one would not expect such behavior in most cases. Unfortunately, the climb would be difficult to detect directly. If the dislocation separation is 10^{-4} cm (i.e., if the dislocation density is 1.2×10^7 lines per cm²), each dislocation climbs only about 10^3 atomic distances in a quench from 700°C.

SUMMARY AND DISCUSSION

To summarize, it appears that the quenching and annealing data for gold can be interpreted by supposing that vacancies are retained and migrate. The energy of formation of vacancies in gold is 0.98 ± 0.04 ev, whereas that of migration is 0.78 ± 0.06 ev. Upon quenching, an appreciable number of divacancies are formed, particularly if the higher temperature is above 850°C. The binding energy of the divacancy is small, being between 0.1 ev and 0.2 ev. The energy of motion of a divacancy does not differ much from that of a single vacancy, being only of the order of 0.1 ev to 0.2 ev less than E_M for a single vacancy.

It is possible that the critical defect which plays the dominant role is a divacancy, rather than a vacancy, and that the trivacancy is the important aggregate. This does not appear to be likely since it would require a rather large value of B that is one near 0.98 ev.

It should also be mentioned that the assignments made here have a bearing on other experiments involving imperfections. For example, Manintveld¹³ deformed gold at 78°K and found two annealing processes having activation energies of 0.29 ev and 0.69 ev. Divacancies cannot be used to explain the 0.29 ev process if they move with an activation energy of the order of 0.6 ev.

APPENDIX

Since the defects do not disappear at dislocations in this approximation, the total number of vacancies present per unit volume is a constant. Thus

$$n = N(c + 2c_2), \quad (A1)$$

where N is the number of atoms per cc. Let Z be the fraction of vacancies that are single and let Z_0 be the

¹² J. Bardeen and C. Herring, *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), p. 261.

¹³ J. A. Manintveld, *Nature* **169**, 623 (1952); J. A. Manintveld, thesis, 1954 (unpublished).

equilibrium value for this fraction. Then, taking $\nu_2' = \nu_2$,

$$Z_0 = \frac{1}{\left(1 + \frac{8\nu}{\nu_2} e^{(B-E_F)/kT_0}\right)} \tag{A2}$$

If $Z = Z_0 + \eta$, η is the change in the fraction of vacancies which are single during the quench. In the cooling process, the time may be replaced by the temperature using the relation $T = T_0 - \beta t$. The resulting equation giving η is

$$\frac{d\eta}{dT} = \frac{16\nu n}{\beta N} (Z_0^2 + 2Z_0\eta + \eta^2) e^{-E_M/kT} - \frac{2\nu_2(1-Z_0-\eta)}{\beta} e^{-(E_M+B)/kT} \tag{A3}$$

If $\eta \ll Z_0$ the nonlinear term in η^2 can be dropped and one finds

$$\eta = \exp\left(\int_{T_0}^T f(T') dT'\right) \times \left\{ \int_{T_0}^T g(T') \exp\left(-\int_{T_0}^{T'} f(T'') dT''\right) dT' \right\}, \tag{A4}$$

where

$$f(T'') = \frac{32\nu}{\beta} \left(\frac{n}{N}\right) Z_0 e^{-E_M/kT''} + \frac{2\nu_2}{\beta} e^{-(E_M+B)/kT''}, \tag{A5}$$

and

$$g(T') = \frac{16\nu}{\beta} \left(\frac{n}{N}\right) Z_0^2 e^{-E_M/kT'} - \frac{2\nu_2}{\beta} (1-Z_0) e^{-(E_M+B)/kT'}. \tag{A6}$$

For values of B in the range from 0.1 eV to 0.3 eV, the second term in $f(T'')$ is an order of magnitude larger than the first, using $E_M = 0.8$ eV and $\nu = 2.25\nu_2$. The first term has therefore been neglected. Introducing

$$\begin{aligned} y &= E_M + B/kT', \\ y_0 &= E_M + B/kT_0, \end{aligned} \tag{A7}$$

one finds that¹⁴

¹⁴ E. T. Whitaker and G. N. Watson, *Course of Modern Analysis* (Cambridge University Press, Cambridge, 1927), p. 352.

$$\int_{T_0}^{T'} f(T'') dT'' = \frac{\nu_2(E_M+B)}{k} \times \left[+\frac{e^{-y}}{y^2} \left(1 - \frac{2}{y} + \frac{6}{y^2} - \frac{24}{y^3} + \frac{120}{y^4} - \dots\right) - \frac{e^{-y_0}}{y_0^2} \left(1 - \frac{2}{y_0} + \frac{6}{y_0^2} - \frac{24}{y_0^3} + \frac{120}{y_0^4} - \dots\right) \right]. \tag{A8}$$

It is important that as few approximations as possible be made for high temperatures, near T_0 . With this in mind, we define:

$$\begin{aligned} z &= e^{-y}/y^2, \\ z_0 &= e^{-y_0}/y_0^2, \end{aligned} \tag{A9}$$

and

$$t = \frac{\nu_2(E_M+B)h_0}{k\beta} = \frac{\nu_2(E_M+B)}{k\beta} \left(1 - \frac{2}{y_0} + \frac{6}{y_0^2} - \frac{24}{y_0^3} + \frac{120}{y_0^4} - \dots\right). \tag{A10}$$

Then if we assume that the final temperature is so low that no motion or divacancy breakup occurs, that is if the final temperature is taken to be 0°K,

$$\int_{T_0}^0 g(T') \exp\left(-\int_{T_0}^{T'} f(T'') dT''\right) dT' = \frac{A(E_M+B)}{y_0^{2s} k(1+2/y_0)} \int_0^{z_0} e^{t(z_0-z)} dz \left(\frac{1}{z_0^s} - \frac{1}{z^s}\right), \tag{A11}$$

where

$$\begin{aligned} A &= (16\nu/\beta)(n/N)Z_0^2, \\ s &= B/(E_M+B). \end{aligned} \tag{A12}$$

The foregoing integral has been evaluated by introducing a new variable $n = tz$. It has been assumed that the upper limit of integration of n can be replaced by infinity. This is a very good approximation for the cases examined here. The resulting value of η is

$$\eta = \frac{32\nu Z_0^2 (E_M+B) r_0^{1-s} e^{-E_M/kT_0}}{y_0^{2s} (1+2/y_0) \beta k (tr_0)} \times \left(1 - \frac{(tr_0)^s (1-s)!}{1-s}\right), \tag{A13}$$

where

$$r_0 = \frac{e^{-y_0}}{y_0^2} \left(1 - \frac{2}{y_0} + \frac{6}{y_0^2} - \frac{24}{y_0^3} + \frac{120}{y_0^4} - \dots\right). \tag{A14}$$