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Quenching and Annealing of Lattice Vacancies in Pure Silver*†

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Quenching and annealing experiments on 99.998% pure silver lead to the following results: The energy required to form a lattice vacancy is 1.10±0.04 eV. The activation energy required to move a lattice vacancy is 0.83±0.05 eV. In specimens quenched from above 600°C most of the defects observed annealed with an activation energy of 0.57±0.03 eV. Pulse heating breaks up the 0.57-eV defect; at least one of the fragments thus produced is a single vacancy having migration energy 0.83±0.05 eV. It is suggested that the 0.57-eV defect is a divacancy. The pulse heating establishes the binding energy of the 0.57-eV defect to be 0.38±0.05 ev. Upon annealing a quenched specimen below 0°C the 0.57-eV defect anneals by second-order kinetics. Upon annealing a quenched specimen above 90°C one observes a fast annealing (approximately first order with energy of motion 0.60±0.06 eV) followed by a slow annealing process having energy of motion 0.80±0.1 eV. It is suggested that above 90°C the 0.57-eV defect does not cluster, but migrates to dislocations. The fact that below 0°C the 0.57-eV defect forms clusters, whereas above 90°C it does not, leads to a binding energy for quadrivacancies of 0.30±0.08 eV.

I. INTRODUCTION

Most of the imperfections present in thermal equilibrium in solids at high temperatures can be frozen-in by rapid cooling. In close-packed metals the dominant imperfections are vacancies, vacancy clusters, and dislocations arising from collapsed vacancy clusters. Interstitials are not as common as vacancies in close-packed metals because they require about three times as much energy to be formed.[1] The first quenching research concerned with lattice defects was done on gold by Kauffman and Koehler.[2] Perhaps the most detailed and precise study on gold was performed by Bauerle and Koehler.[3]

Previous to our experiment, other quenching experiments were done on materials which remain pure upon heating in air. Some of these materials are gold, aluminum,[4] and platinum.[5] The present research extends this work to materials which become contaminated in air. Silver was chosen because it is close-packed and monovalent and therefore can be interpreted theoretically more easily than most metals. Also there exist excellent self-diffusion measurements done on silver.[6]

II. EXPERIMENTAL PROCEDURE

A. Specimen Preparation and Mounting

Specimen material for this experiment was Johnson and Matthey 99.999% pure 1.2-mm diameter silver rod, catalog No. J.M. 52. Some earlier wires used were drawn by the Sigmund Cohn Corporation, Mount Vernon, New York. The purity of the wires drawn by us was higher than that of wires drawn by the Sigmund Cohn Corporation.

Initially 16-mil silver wire was quenched in water as in the method of Bauerle and Koehler[3] except that the specimen was heated under a purified argon atmosphere. Because of the presence of water vapor and impurities in the atmosphere, good reproducible data could not be obtained.

After several methods were tried, the following successful technique was evolved. Two-mil silver wires and a tantalum ribbon getter were sealed into a Corning 7720 or 7740 glass tube. The tube was evacuated to 1×10^{-9}mm Hg by a bakable ultra-high vacuum system. It was then filled with Linde M.S.C. (mass spectrometer controlled) helium. Current leads and potential leads were brought out of the tube through tungsten wires sealed in Corning 7720 glass. The helium gas inside the tube was cleaned each time the specimen was heated by first heating the getter. Heating was accomplished by passing direct current through the getter. While the silver wire or the getter was being heated the tube was kept horizontal in a liquid nitrogen bath.

In earlier variations of this experiment, the specimen and a symmetrically arranged dummy were mounted as shown in Fig. 1. The gauge length was about 8 cm. The specimen and the matched dummy were heated to 800°C for 30 min while horizontal. During this time the tube was immersed in a liquid nitrogen bath. The specimen and dummy were then cooled slowly. The residual resistivity was between $2\times10^{-9}\Omega$ cm and $6\times10^{-9}\Omega$ cm depending upon miscellaneous factors (the purity of wire after drawing, vacuum before sealing, cleanliness of the tube, etc.). Best results were obtained

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† This paper is based upon a dissertation submitted by Masao Doyama in partial fulfillment of the requirements for the Ph.D. Degree at the University of Illinois.

[1] H. B. Huntington, Phys. Rev. **91**, 1092 (1953); H. B. Huntington and F. Seitz, *ibid.* **61**, 315 (1942); H. B. Huntington, *ibid.* **61**, 325 (1942); H. Brooks, *Impurities and Imperfections* (American Society for Metals, Cleveland, Ohio, 1955).

[2] J. W. Kauffman and J. S. Koehler, Phys. Rev. **88**, 149 (1952); *ibid.* **97**, 555 (1955); J. W. Kauffman, thesis, University of Illinois, 1955 (unpublished).

[3] J. E. Bauerle, C. E. Klabunde, and J. S. Koehler, Phys. Rev. **102**, 1182 (1956); J. E. Bauerle and J. S. Koehler, *ibid.* **107**, 1493 (1957); J. E. Bauerle, thesis, University of Illinois, 1957 (unpublished).

[4] W. Desorbo and D. Turnbull, Acta Met. **7**, 83 (1959); Phys. Rev. **115**, 560 (1959); F. J. Bradshaw and S. Pearson, Phil. Mag. **2**, 570 (1957); C. Panseri and T. Federighi, Phil. Mag. **3**, 1223 (1958).

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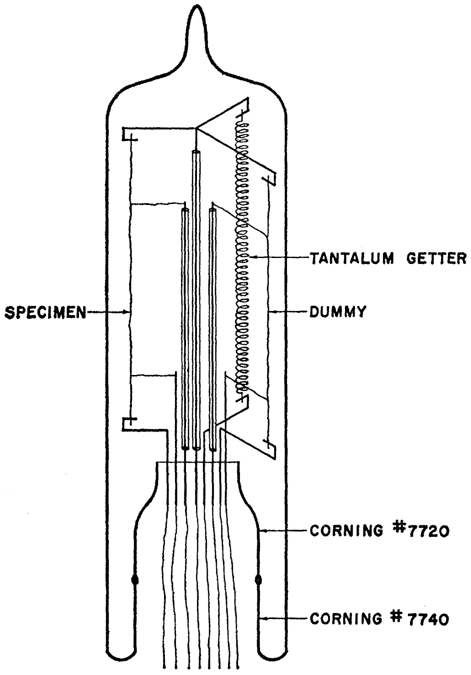

FIG. 1. Schematic drawing of specimen tube.

when the tube was baked (at 450°C for 8 h) several times under a vacuum before the specimen was mounted. The tube was baked at 450°C for 30 min after the specimen was mounted.

B. Quenching, Annealing, and Pulsing

The specimen was quenched by the method developed by Jackson and Koehler[7], i.e. by turning off 93% of the current with the wire in an atmosphere of helium gas cooled through the tube wall by liquid nitrogen. The quench curve was recorded using an oscilloscope by the method of Kauffman and Koehler[2] and was closely exponential. The time required for the specimen temperature to drop half way to liquid nitrogen temperature was from 14 to 20 msec. The specimen was cooled principally by convection and slightly by radiation.

Annealing studies were made by transferring the tube to an alcohol bath cooled with dry ice or to a water or oil bath containing heaters. The temperature of the bath was controlled to ±0.02°C for temperatures below 0°C and to ±0.01°C for temperatures above 0°C. Short anneals at high temperatures were accomplished by passing direct current through the specimen. When this was done the tube was supported horizontally in liquid nitrogen.

After some quenches a short temperature pulse in the specimen was produced by passing current through it momentarily. The heating curve was recorded using an oscilloscope.

C. Resistivity Measurements

Changes in residual resistivity of the specimen were measured by immersing the specimen tube in liquid helium to minimize the temperature-dependent part of the electrical resistivity because quenched-in resistivity was rather small.

The method used for measuring resistivity was rather simple. Current and voltage across the specimen were measured at the same time. For stability of the current, six Willard Low Discharge type DH-5-1 batteries were connected as follows. Three banks of batteries were connected in parallel, each bank consisting of two batteries in series. Three banks of resistors in parallel, each bank consisting of one decade resistor and one precision wire wound resistor in series were used to adjust the current through the specimen to a desired value. In this manner the current was held at the desired value to within one part in a few hundred thousandths. The value of the current was determined by measuring, by means of a Leeds and Northrup type K-2 potentiometer, the voltage across a Rubicon 1-Ω standard resistance connected in series with the specimen. The voltage across the specimen was mesaured by a Rubicon thermofree microvolt potentiometer (Rubicon catalog No. 2767) in conjunction with a Rubicon photoelectric galvanometer (Rubicon catalog No. 3550). The voltage across the gauge length of the specimen could be read to 0.001 μV. The thermal electromotive force in the circuit (of the order of 0.2 μV) was canceled by averaging a reading of the current in one direction

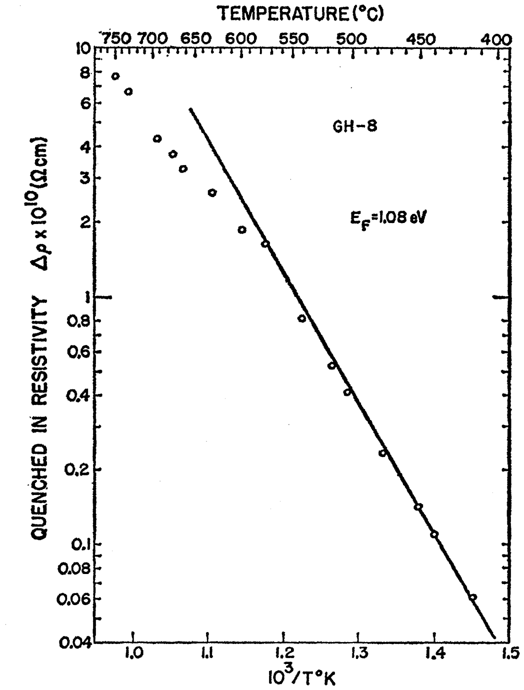

FIG. 2. Semilogarithmic plot of quenched-in resistivity vs reciprocal of the absolute quench temperature.

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[7] J. J. Jackson, thesis, University of Illinois, 1960 (unpublished); J. J. Jackson and J. S. Koehler (to be published).

with a reading of the current in the opposite direction. Although the smallest detectable change in resistivity was $3\times10^{-14}\Omega$cm, the observed error was a little less than $1\times10^{-12}\Omega$cm. The difference was due largely to the fluctuations of thermal emf in the circuit.

Earlier measurements of resistivity were made at liquid nitrogen temperature by the bridge technique developed by Kauffman and Koehler. Some improvements were required to measure very small changes in resistivity. The principal improvements were as follows. Two 50-Ω standard resistors were used instead of two 1-Ω standard resistors so that the current stability and the balance of the bridge $(I_S=I_D)^2$ were improved. A Rubicon photoelectric galvanometer was also used to balance the bridge. The smallest resistivity change detectable was $3\times10^{-14}\Omega$cm. In spite of the above improvements the largest error resulted from the temperature difference between the specimen and the dummy which were indirectly cooled by liquid nitrogen. The observed error was $5\times10^{-12}\Omega$cm.

III. RESULTS

A. Quenching

The increase in resistivity quenched in the specimen upon cooling from temperature T_Q is given by

$$\Delta\rho=A\exp(-E_F/kT_Q), \tag{1}$$

where A is a constant, E_F is the energy required to form the defect, and k is Boltzmann's constant. Some of the results are shown in Fig. 2. The average results were $E_F=1.10\pm0.04$ eV, $A=(4.5\pm1.5)\times10^{-4}$ Ωcm. A bending in the curve was observed for quenching temperatures above 650°C. This deviation occurred because (1) the quenching rate was not rapid enough, (2) the wire was thin, and (3) the energy of motion of the defects was low in comparison with the values observed in gold. The time required to cool to one-half of the absolute quenching temperature was 17±3 msec. This time was determined by the helium pressure inside the tube. In earlier data,[8] A was found to be different in different specimens, even though E_F was almost the same. This was probably a consequence of the fact that the specimen length was too short to determine accurately the absolute value of the quenched-in resistance.

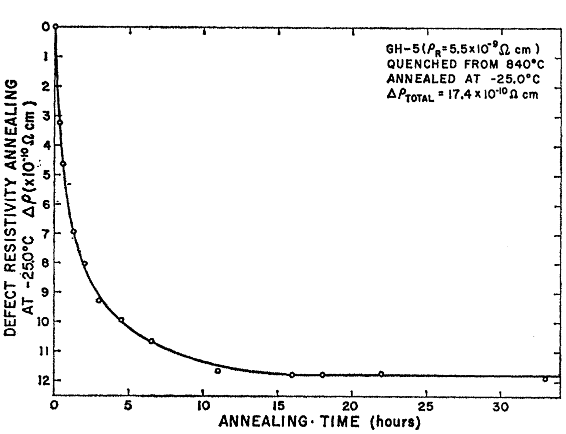

FIG. 3. Defect resistivity annealing at −25.0°C vs time. Quench temperature was 840°C.

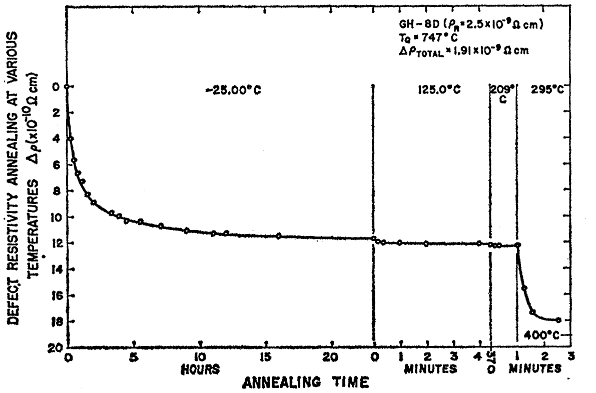

FIG. 4. Defect resistivity annealing at −25.0, 125.0, 209.0, 295, and 400°C vs annealing time. Quench temperature was 747°C. Total quenched-in resistivity was $1.91\times10^{-9}\Omega$cm, and residual resistivity after annealing was $2.5\times10^{-9}\Omega$cm.

B. Annealing

The annealing behavior of quenched-in resistivity was found to depend upon annealing temperature and upon thermal treatment given after the quench but before the anneal. The annealing studies were carried out at annealing temperatures below 0°C and above 90°C because it was found that the annealing kinetics are quite different in these temperature ranges.

1. *Annealing below 0°C*

In a specimen freshly quenched from temperatures between 850 and 580°C, a rapid anneal (a few minutes) was observed near 10°C. Considerable annealing data were therefore obtained between −50°C and 0°C.

(a) Some of the annealing curves giving $\Delta\rho$ vs annealing time are plotted in Figs. 3 and 4. In Fig. 5, values of $1/(\Delta\rho-\Delta\rho_\infty)$ vs annealing time are plotted. Here $\Delta\rho$ is the quenched-in resistivity at time t, $\Delta\rho_\infty$ is the quenched-in resistivity after annealing for a long time (23 h at −25.0°C). The annealing of the quenched-in resistivity showed second-order reaction kinetics which can be represented by the equation

$$d(\Delta\rho)/dt=-\alpha_\rho(\Delta\rho)^2, \tag{2}$$

where α_ρ is a function of the annealing temperature. Slight deviations from the second-order law were found after more than 90% of the resistance increment had annealed. In this stage the annealing rate was faster than expected for a second order process.

(b) The time τ required for one half of the resistivity to disappear by the annealing process was 48 min at

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[8] M. Doyama and J. S. Koehler, Phys. Rev. **119**, 939 (1960).

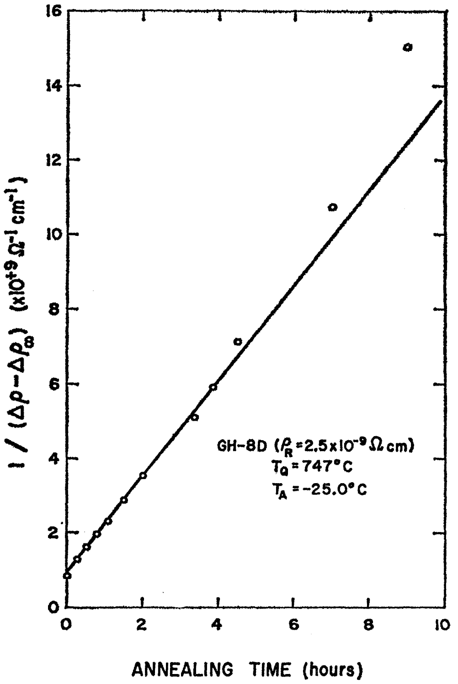

FIG. 5. $1/(\Delta\rho-\Delta\rho_\infty)$ vs time annealed at -25°C, where $\Delta\rho$ is defect resistivity after time t and $\Delta\rho_\infty$ is defect resistivity after infinite time. Quench temperature was 747°C.

-25.0°C. Figures 4 and 5 pertain to a specimen quenched from 747°C.

(c) To determine the activation energy for motion of a defect E_M, it was always assumed in these experiments that

$$dc/dt=-f(c)\exp(-E_M/kT_A), \tag{3}$$

where c is the concentration of the defect, and T_A is the annealing temperature. The increase in resistivity is taken to be proportional to the concentration of the defect.[3] Using this relation one finds that

$$d(\Delta\rho)/dt=-\beta_\rho f(\Delta\rho)\exp(-E_M/kT_A), \tag{4}$$

where β_ρ is a constant for a given specimen.

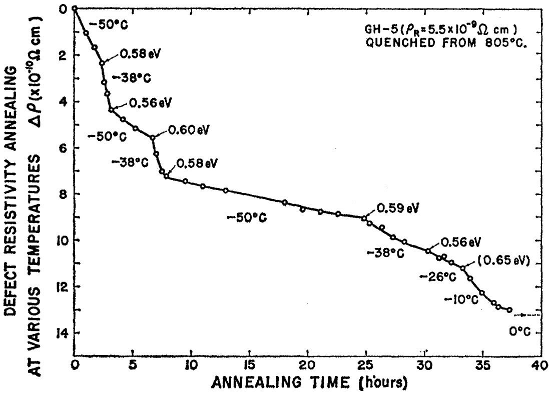

FIG. 6. Energy of motion determination for a specimen quenched from 805°C and annealed at -50.0, -38.0, -26.0, and -10.0°C.

The activation energy for motion of the defect which moves during anneals at temperatures below 0°C was computed to be 0.57 ± 0.03 eV using the following relations:

(i) (Fig. 6)

$$\left(\frac{dc}{dt}\right)_1\bigg/\left(\frac{dc}{dt}\right)_2=\exp\left\{-\frac{E_M}{k}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right\}; \tag{5}$$

(ii) (Fig. 7)

$$\frac{\alpha\rho_1}{\alpha\rho_2}=\exp\left\{-\frac{E_M}{k}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)\right\}; \tag{6}$$

(iii) (Fig. 8)

$$d(\Delta\rho)/dt=-\gamma_\rho\exp(-E_M/kT_A), \tag{7}$$

(at constant concentration). Note that Eq. (5)–(7) assume that the annealing rates at different temperatures are compared for the same concentrations of the moving defect.

(d) The quenched-in resistivity did not completely anneal out at temperatures between -50 and 0°C. We will call the quenched-in resistivity after a prolonged anneal "remaining resistivity" R_R. The higher the annealing temperature, the smaller R_R. For the specimen quenched from 840°C, R_R was about 40% of the total quenched-in resistivity near 0°C.

A fraction of the remaining resistivity R_R can be annealed out at high temperatures. Figure 9 shows the

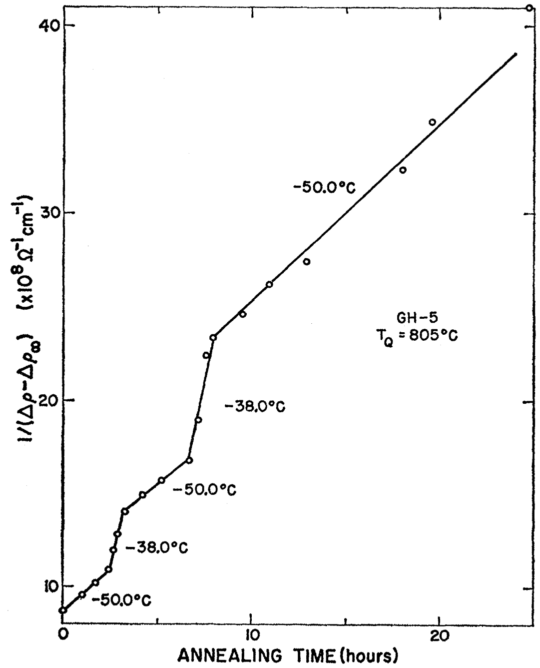

FIG. 7. $1/(\Delta\rho-\Delta\rho_\infty)$ vs time annealed at -50.0 and -38.0°C, where $\Delta\rho$ is the defect resistivity after time t and $\Delta\rho_\infty$ is the defect resistivity after infinite time. Quench temperature was 805°C.

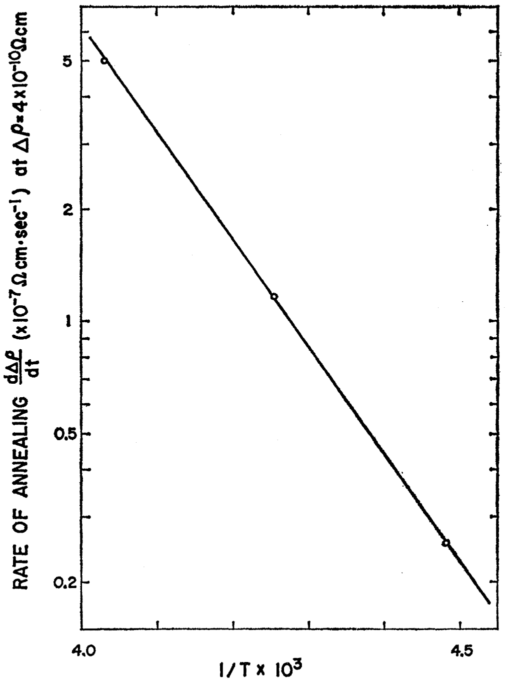

FIG. 8. Semilogarithmic plot of rate of annealing at defect resistivity $\Delta\rho = 4\times10^{-10}\Omega$cm vs reciprocal of the absolute annealing temperature.

variation of the remaining resistivity with increasing annealing temperature. This specimen was quenched from 840°C and was annealed at −25.0°C for 33 h; thereafter the specimen was heated to successively higher temperatures. It was held at each temperature until a metastable state characteristic of that temperature was obtained, i.e., 10 h at temperatures below 100°C, about 1 h at temperatures between 100 and 200°C, and 5 min at temperatures above 200°C.

(e) Some specimens were heated in a helium gas pocket in liquid helium to avoid any contamination due to oxygen. Annealing by this method was essentially the same as described above. But because the consumption of liquid helium was 1 liter/min when the specimen was heated, this method was used only long enough to check the above results.

2. *Annealing above 90°C*

If, after quenching, a specimen was immediately annealed at temperatures above 90°C, two stages of annealing were observed—an initial fast process and a later slow process.

(a) In the initial fast process the time τ required to anneal half of the quenched-in resistivity did not depend much upon quenching temperature. τ was 4 sec at 90.3°C (See Fig. 10). The activation energy associated with the fast annealing process was 0.60±0.06 eV.

(b) Later a slow annealing process became apparent. The half-time τ_2 for this process was about 10 min at 158°C. The activation energy associated with this process was 0.8±0.1 eV.

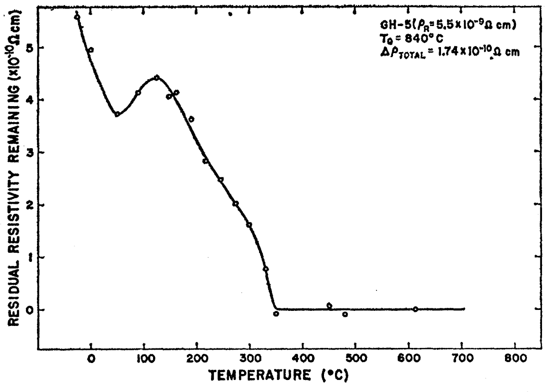

FIG. 9. Residual resistivity remaining after prolonged annealings vs annealing temperatures.

(c) The resistivity remaining after such high-temperature annealing was small. About 5% of the total quenched-in resistivity remains in a specimen quenched from 845°C. This remaining resistivity anneals out at temperatures in the range between 250 and 400°C.

C. Pulsing

A specimen quenched from near 750°C was pulsed to a given temperature between 240 and 465°C for a short time (between 0.01 and 0.1 sec). After a pulse the specimen was annealed near 110°C.

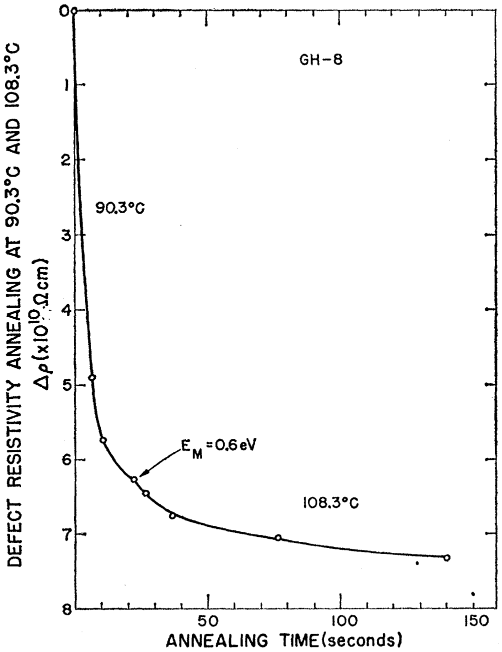

FIG. 10. Energy of motion determination for a specimen quenched from 758°C and annealed at 90.3°C and 108.3°C.

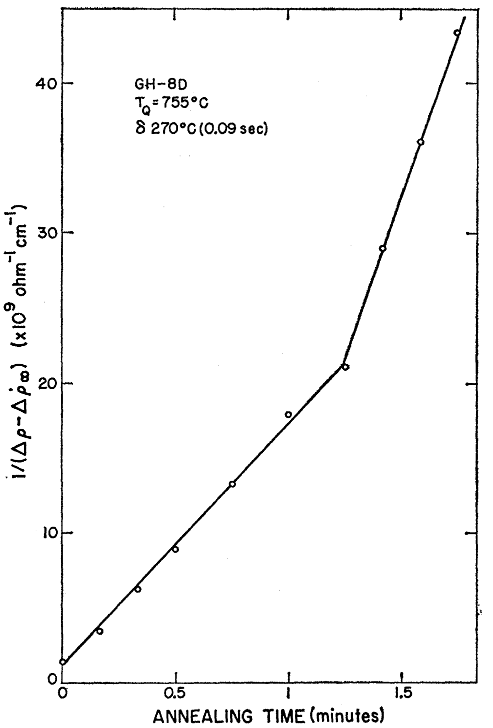

FIG. 11. Energy of motion determination for a specimen quenched from 755°C, pulsed at 270°C for 0.09 sec, and annealed at 113.3°C and 130.0°C.

(a) The annealing of the quenched-in resistivity after an optimum pulse (270°C, 0.09 sec) showed second-order kinetics (see Fig. 11). If the pulse temperature was much higher or much lower than the optimum pulse temperature, the kinetics deviated from second order. In these cases some fast annealing occurred.

(*b*) The apparent activation energy for motion of the defects was determined by annealing the specimen at 110°C for 1.25 min and then annealing it at 130°C E_M was 0.83±0.07 eV for the optimum pulse (270°C, 0.09 sec). E_M was 0.72±0.05 eV for the low pulse (250°C, 0.01 sec). E_M was 0.82±0.07 eV for a high pulse (465°C 0.1 sec and 350°C, 0.1 sec).

(c) The remaining resistivity R_R was about 5% of the total quenched-in resistivity. R_R began to decrease appreciably at 250°C and completely disappeared at 400°C. At 330°C, it was necessary to heat the specimen about 10 sec to obtain a metastable state.

IV. INTERPRETATION AND DISCUSSION

A. Introduction

Quenching experiments are important for the following reasons. (1) They provide one of the simplest methods to study imperfections in solids. They are simple because quenching produces mainly lattice vacancies or vacancy clusters in close-packed metals, (2) The quenching experiments give information concerning the defect which is responsible for self-diffusion in pure silver.

Quenching experiments performed on gold[3] and aluminum,[4] when combined with the work of Simmons and Balluffi[9], established that the vacancy mechanism of diffusion proposed by Huntington and Seitz[10] is probably the correct mechanism in close-packed lattices.

The theory of quenching and the annealing behavior of quenched-in defects is treated by Koehler, Seitz, and Bauerle.[11] The differential equations which govern the concentration of defects are given in their paper.

B. Aims

One would like to answer the following questions with the data of these experiments:

(1) What is the energy required to form a lattice vacancy in silver?

(2) How much does electrical resistivity increase if 1% of the lattice sites are vacant?

(3) What kind of imperfections does one have after a quench?

(4) What is the energy required to move a single vacancy?

(5) What is the energy required to move a divacancy?

(6) What are the annealing kinetics of the defects? Specifically, where do they go during the annealing process?

C. Quenching

The value of the energy of formation of a lattice vacancy E_F found in this experiment is in excellent agreement with the value found by Simmons and Balluffi[9] who measured the equilibrium concentration by the lattice parameter and length method at a succession of high temperatures. Using their value for the vacancy concentration at the melting point of silver together with an extrapolation to the melting point of the curve in the present research, one obtains $\Delta\rho(1\%) = (1.3\pm0.7)\,\mu\Omega$ cm, where $\Delta\rho$ (1%) represents the resistivity increment produced if 1% of the lattice sites are vacant and if most of the voids are present as divacancies.

Koehler, Seitz, and Bauerle[1] showed that the divacancy concentration produced during a quench can be large if the binding energy B_{Di} between two single vacancies is large. As will be shown later, this is the case in silver. Most of the quenched-in defects retained in the specimen are divacancies; some are possibly higher complexes or dislocations.

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[9] R. O. Simmons and R. W. Balluffi, Phys. Rev. **119**, 600 (1960).

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

[11] J. S. Koehler, F. Seitz, and J. E. Bauerle, Phys. Rev. **107**, 1499 (1957).

D. Annealing

1. Annealing at Temperatures below 0°C

Three facts indicate that most defects do not go to dislocations in silver annealed at temperatures below 0°C. First, the resistivity remaining after a prolonged anneal below 0°C is high. Second, the reaction kinetics are second order as shown by the annealing behavior at these temperatures. Third, during annealing, the number of jumps determined experimentally is much smaller than that expected if defects went only to dislocations. The number of defect jumps n_j in time τ is given by

$$n_j = 4\tau\nu \exp(-E_M/kT_A). \tag{8}$$

From Fig. 4 or 5, the annealing half-time τ is found to be 48 min at -25.0°C in the specimen quenched from 747°C. The number of jumps in this case is 7.4×10^4. The number of jumps required on the average for a defect to reach a dislocation in the specimen used is of the order of 10^6 (see Sec. 3 below).

The activation energy expected for the motion of single vacancies in silver, if self-diffusion occurs by the vacancy mechanism, is 0.82 eV ($E_M{}^V = E_{\text{diff}} - E_F{}^V = 1.92 - 1.10 = 0.82$ eV. The activation energy for self-diffusion E_{diff} was measured by Tomizuka and Sonder[6]. The value found in the present annealing was 0.57 eV which is much smaller than the value expected for single vacancies. Therefore, the defects which move at temperatures below 0°C are probably not single vacancies but are instead some kind of cluster.

2. Formation of Complexes

The resistivity remaining after a prolonged anneal below 0°C was much higher (40%) than that remaining after a prolonged anneal near 110°C (5%). It is supposed that most of the defects which move below 0°C do not disappear completely but remain in the form of larger vacancy complexes. Because the behavior of the anneal shows second-order reaction kinetics, most of the remaining resistivity probably consists of pairs of the defect. "The second stage" in the annealing of aluminum found by Panseri and Federighi[4] probably corresponds to our remaining resistivity.

The deviation from second-order kinetics during later stages of the anneal (see Fig. 5) could be explained if the pairs of defects absorb additional defects thus making larger complexes, or if the defects go to dislocations in these stages. This would produce a deviation toward first-order kinetics, giving more rapid annealing than predicted. Such a deviation is observed.

3. Annealing above 90°C

The activation energy for motion of the defects in a freshly quenched specimen is again about 0.57 eV in the early stages of annealing. This shows that the defects which move at temperatures below 0°C also move at temperatures above 90°C. However, the resistivity remaining after a prolonged anneal above 90°C is much smaller than that observed in the same specimen quenched from the same temperature but annealed below 0°C. These facts indicate that the defects which move do not make pairs at temperatures above 90°C or at least that the breakup time of a pair is short compared with the half-time of the annealing process. The half-time at 90.3°C was 4 sec. This implies that 2×10^6 jumps occur. One can conclude that most of the defects go to dislocations at temperatures above 90°C. In other specimens prepared in the same way, the number of jumps required varied by a factor of 2 or 3.

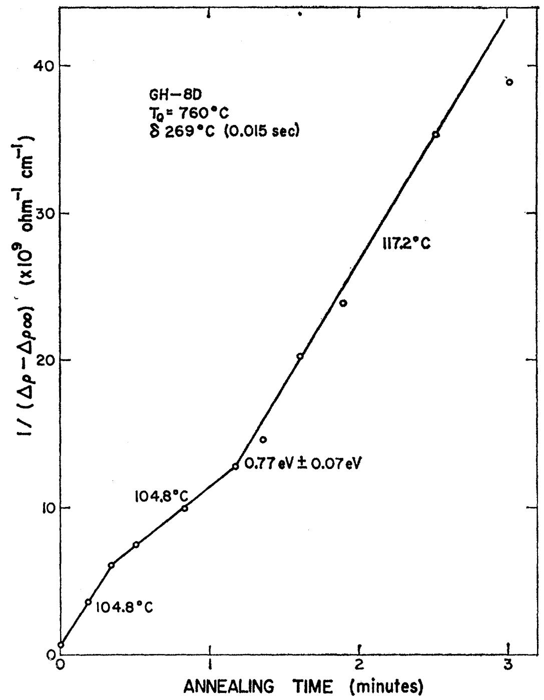

FIG. 12. Energy of motion determination for a specimen quenched from 760°C, pulsed near 270°C for approximately 15 msec, and annealed at 104.8 and 117.2°C.

E. Pulsing

Short temperature pulses were given after a quench to break up the defect moving with the activation energy of 0.57 eV.

(1) A short pulse (270°C for approximately 15 msec.) did not break up all the defects. The specimen was quenched from 760°C; the resistivity increment quenched in was $\Delta\rho_Q = 15.00\times10^{-10}\ \Omega$ cm; the resistivity increment remaining after the pulse was 12.31×10^{-10} Ω cm. Subsequent annealing at 104.8°C revealed two stages as shown in Fig. 12. The first stage probably resulted from divacancy annealing. It accounted for 87% of the resistivity increment. The remaining defect resistivity annealed according to second order kinetics. Its activation energy was determined by changing the

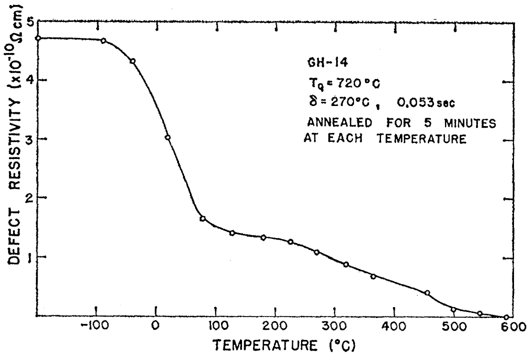

FIG. 13. Defect resistivity of isochronal annealing for 5 mins at each of the temperatures. $T_Q=720°\text{C}$, $\Delta\rho_Q=10.3\times10^{-10}\Omega\text{cm}$, and $T_p=270°\text{C}$ for 0.053 sec.

annealing temperature and was 0.77 ± 0.07 eV. The remaining defects were probably single vacancies.

(2) An optimum pulse (270°C, 0.09 sec) broke up all of the defects but did not lose many defects. The specimen was quenched from 755°C; $\Delta\rho_Q=13.57\times10^{-10}$ Ω cm. The resistivity increment remaining after the pulse was 7.36×10^{-10} Ω cm. The annealing at 113.3°C and 130.°C after the pulse follows second-order kinetics as shown in Fig. 11. The defect moves with an activation energy of $E_m=0.83\pm0.05$ eV which indicates that it is a single vacancy. Apparently two single vacancies combine to form divacancies which then migrate very rapidly in comparison with the single vacancy.

(3) High-temperature pulses (350°C, 0.1 sec and 465°C, 0.1 sec) also produced single vacancies since the resulting activation energy for motion was 0.82 ± 0.04 eV. However, a large part of the quenched-in resistivity was lost during the pulse.

Let us attempt to describe pulsing under the assumption that during the pulse the loss of defects to dislocations is negligible. Then:

$$dc_1/dt=-6\nu_1c_1^2\exp(-E_M{}^V/kT)+2\nu_2c_2\exp[-(E_M{}^V+B_{\text{Di}})/kT]=2Ac_1^2+2Fc_2 \quad (9)$$

and

$$c_1+2c_2=c_{10}=\text{const.} \quad (10)$$

Here c_1 and c_2 are the fractional concentration of vacancies and divacancies, ν_1 and ν_2 are the frequencies with which atoms next to a vacancy and a divacancy vibrate. $E_M{}^V$ is the activation energy for vacancy migration and B_{Di} is the binding energy of a divacancy. c_{10} is the total concentration of vacancies including both singles and divacancies present at the end of the pulse. The solution of Eqs. (9) and (10) appropriate here is

$$c_1=\tfrac{1}{2}\left[(F/2A)\left(\frac{F}{2A}+4c_{10}\right)\right]^{\frac{1}{2}}\tanh\left\{\left[(AF/2)\left(\frac{F}{2A}+4c_{10}\right)\right]^{\frac{1}{2}}(t+t_0)\right\}-F/4A, \quad (11)$$

where t_0 is chosen to fit the initial condition. The pulse data must fit two conditions. First, the time constant must be correct and second, the resulting long-time equilibrium value of c_1 must be that given by experiment. In the case of the 270°C pulse for 0.09 sec, both conditions are consistent with a value of B_{Di} which is $B_{\text{Di}}\leqslant0.37$ eV. This result is at least roughly consistent with the short quench data. A more stringent test is furnished by data on a specimen pulsed to 270°C for 0.053 sec. Figure 13 shows the results of isochronal annealing for 5 min at each of the temperatures specified. If one calculates the number of jumps made by a single vacancy and by a divacancy during 5 min at the lowest temperatures used, one finds ($E_M{}^V=0.83$ eV, $E_M{}^{\text{Di}}=0.57$)

	n_{j1}	n_{j2}
−90°C	2.5×10^{-7}	0.4
−35°C	4.8×10^{-2}	1.70×10^{3}
18°C	7.6×10	2.68×10^{5}
77°C	2.0×10^{4}	1.24×10^{7}

The figures indicate that the pronounced drop which occurs during annealing at 18° and 77°C can only arise from divacancy motion. If one supposes that 40% or more of the vacancies are present as divacancies and if the resistivity increments produced by 1% vacancies and if the divacancies are both 1.3×10^{-6} Ω cm, then using (11) one finds that $B_{\text{Di}}\geqslant0.38$ eV. One therefore can set $B_{\text{Di}}=0.38\pm0.05$ eV.

The increase of apparent activation energy for motion of defects cannot be explained by the selective annealing of divacancies because during an optimum pulse a divacancy makes 10^7 jumps which is one order higher than the estimated number of jumps during annealing near 100°C. It is of course conceivable that the sinks are less effective at high temperature.

F. Divacancy Annealing

The frequency with which a lattice vacancy jumps into a neighboring lattice site ω_V and the diffusion constant D_V associated with single vacancies at a temperature T_A are given by

$$\omega_V=12\nu_V\exp[-E_M{}^V/(kT_A)], \quad (12)$$

$$D_V=\nu_Va^2\exp[-E_M{}^V/(kT_A)], \quad (13)$$

where ν_V (of the order of 10^{13}/sec) is the frequency with which atoms next to a vacancy vibrate. $E_M{}^V$ is the activation energy for motion of a single vacancy. For a divacancy the corresponding expressions for frequency and diffusion constant are

$$\omega_{\text{Di}}=4\nu_2\exp(-E_M{}^{\text{Di}}/kT_A); \quad (14)$$

$$D_{\text{Di}}=\tfrac{1}{6}\nu_2a^2\exp(-E_M{}^{\text{Di}}/kT_A). \quad (15)$$

The ratio of the diffusion constant of a divacancy to that of a single vacancy is

$$D_{\text{Di}}/D_V=(\nu_2/6\nu_V)\exp[(E_M{}^V-E_M{}^{\text{Di}})/kT_A]. \quad (16)$$

Assuming $\nu_2=\nu_1=10^{13}$, $E_M{}^V=0.83$ and $E_M{}^{\mathrm{Di}}=0.57$ eV at -25.0°C, we obtain

$$D_{\mathrm{Di}}/D_V=1.2\times10^5.$$

Therefore, if single vacancies and divacancies were present in equal concentrations at -25°C, the annealing would occur overwhelmingly by divacancy motion. In fact, the single-vacancy concentration would have to exceed the divacancy concentration by a factor of 1.2×10^5 to achieve equal annealing rates by single vacancies and divacancies. One therefore suspects that annealing below 0°C occurs by the motion of divacancies.

Let us consider the process in which two divacancies meet to form a quadrivacancy. The number of quadrivacancies formed per second is

$$dC_{\mathrm{Di}}/dt=-G\nu_2C_{\mathrm{Di}}{}^2\exp(-E_M{}^{\mathrm{Di}}/kT_A), \tag{17}$$

where ν is a frequency factor, C_{Di} is the concentration of divacancies, and G is a dimensionless geometrical constant having a value of the order of one. Integration of Eq. (17) yields

$$\frac{1}{C_{Di}}-\frac{1}{C_{Di_0}}=G\nu_2t\exp\left(-\frac{E_M{}^{Di}}{kT_A}\right), \tag{18}$$

where C_{Di0} is the initial concentration of divacancies. Figure 5 gives a value of G equal to 1.7. G was found experimentally to be a constant for each specimen and independent of the quenching temperature. G was between 0.9 and 1.7 for the specimens examined here.

The important role of impurities in trapping vacancies was pointed out by Lomer and Cottrell.[12] Damask and Dienes[13] have also treated vacancy impurity trapping and deduced the resulting annealing kinetics. Experimentally, the lower the residual resistivity, the higher G is. Qualitatively this can be understood if divacancies are trapped by impurity atoms. The time required for a divacancy to make an atomic jump is given by

$$1/t_1=(\nu_2/g_1)\exp(-E_M{}^{\mathrm{Di}}/kT_A), \tag{19}$$

where g_1 is a geometrical constant. Let the binding energy between a divacancy and an impurity atom be B_i. Then the time required to dissociate an impurity and a divacancy is given by

$$1/t_2=(\nu_2/g_2)\exp[-(E_M{}^{\mathrm{Di}}+B_i)/kT_A], \tag{20}$$

where g_2 is a geometrical constant. The probability that a divacancy will associate with impurities within n jumps is nC_i, where C_i is the concentration of impurities. Thus, the total time for a vacancy to make n jumps in a crystal having impurities is

$$t=\frac{g_1n(1-C_i)}{\nu_2}\exp\left(\frac{E_M{}^{Di}}{kT_A}\right)+\frac{nC_ig_2}{\nu_2}\exp\left(\frac{E_M{}^{Di}+B_i}{kT_A}\right). \tag{21}$$

Hence, Eq. (16) can be modified as follows:

$$\frac{1}{C_{Di}}-\frac{1}{C_{Di_0}}=G_i\nu_2t\exp\left(-\frac{E_M{}^{Di}}{kT_A}\right). \tag{22}$$

Here G_i is given by

$$G_i=G/[g_1(1-C_i)+g_2C_i\exp(B_i/kT_A)]. \tag{23}$$

When $C_i\ll1$, this can be written

$$G_i\approx G/[g_1+g_2C_i\exp(B_i/kT_A)]. \tag{24}$$

One finds that B_i is about 0.25 eV, using $G_i\approx G_2$ and assuming $C_i\approx10^{-5}$. Physically, one can see that G should decrease as C_i increases. The higher the impurity concentration, the more time a divacancy spends next to impurity atoms.

The annealing kinetics follow a second-order process. This indicates that two defects of the same kind meet to form an immobile defect. If defects go to impurity atoms the kinetics should not be second order.

In the annealing process below 0°C the remaining resistance was high (40%), and the annealing kinetics were second order. This shows that the breakup time of a quadrivacancy into two divacancies is much longer than the annealing half-time below 0°C. This sets a lower limit of 0.22 eV on the binding energy of a quadrivacancy relative to two well-separated divacancies. At 90°C, on the other hand, either divacancies do not make quadrivacancies, or the breakup time for a quadrivacancy is much shorter than the annealing half-time. This limits the binding energy of two divacancies to a value less than 0.38 eV.

G. Resistivity Remaining after a 120°C Anneal

The resistivity remaining after a prolonged heating near 120°C anneals out in the temperature range between 250 and 400°C. At 330°C the half time required to obtain a metastable state is 10 sec. The time required for annealing is too long to suggest that the breaking up of a simple defect, such as a pentavacancy, determines the lifetime—unless the binding energy is very large, i.e., 0.9 eV.

Isochronal annealing for 5 min at a succession of temperatures shows that one half of the resistivity of the second stage anneals out near 350°C. Using the relation $1/\tau=\nu\exp(-E/kT)$, this gives an activation energy of 1.92 eV which is the same as the activation energy for self diffusion in silver.

The most plausible interpretation of the remaining resistivity is that it arises from dislocation loops or tetrahedral dislocations which form during the 120°C anneal. Such dislocations have been observed in quenched and subsequently annealed silver by Smallman and Westmacott[14] using an electron microscope. We suggest that near 350°C the defects causing the

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[12] W. M. Lomer and A. H. Cottrell, Phil. Mag. **46**, 711 (1955).

[13] A. C. Damask and G. J. Dienes, Phys. Rev. **120**, 99 (1960).

[14] R. E. Smallman and K. H. Westmacott, J. Appl. Phys. **30**, 609 (1959).

remaining resistivity evaporate vacancies and finally disappear.

H. Contribution of the Divacancy to Self-Diffusion in Silver

The formation energy of a single vacancy is 1.10 eV. The binding energy of two single vacancies is approximately 0.38 eV. Thus the formation energy of a divacancy is $1.10\times 2-0.38=1.82$ eV. The experiments show that the activation energy for motion of the divacancy is 0.57 eV. Therefore, the activation energy of self-diffusion should be 2.39 eV if self-diffusion occurs by the motion of divacancies.

The equilibrium fractional concentration of divacancies at 960°C will be 2.5×10^{-6} if we use the relation $C_{\mathrm{Di}}=(6\nu_V C_V{}^2/\nu_2)\exp(B/kT$ with $B=0.40$ eV. This is only 1.5% of the fractional concentration of single vacancies in equilibrium at the same temperature.

At the melting point the ratio of the diffusion constant arising from single vacancies to that from divacancies is

$$\frac{D_{Di}}{D_V}=\frac{C_{Di}\frac{2}{3}\nu_2 a^2\exp(-E_M{}^{Di}/kT)}{C_V\nu_V a^2\exp(-E_{MV}/kT)}\approx 0.077.$$

Thus, the effect of divacancies should be nearly detectable in the vicinity of the melting point.

I. The Solubility of Oxygen in Silver

Steacie and Johnson measured the solubility and the rate of solution of oxygen in silver.[15] They gave the equilibrium concentration of oxygen in silver at 700°C as

$$C_{700°\mathrm{C}}=9.8\times 10^{-6}\sqrt{p}, \tag{25}$$

where p is the partial pressure of oxygen in centimeters of mercury. To check the solubility in silver of oxygen under a low pressure, a 16-mil silver wire, the residual resistivity of which was $7\times 10^{-10}\Omega$ cm, was heated in oxygen for one hour at 700°C and then again for 10 sec at 400°C to anneal only vacancies. The change in electrical resistivity was $-0.6\times 10^{-10}\Omega$ cm and $1.0\times 10^{-10}\Omega$ cm for oxygen pressures of 7.3×10^{-2}mm Hg and 2.3 mm Hg, respectively. The electrical resistivity dropped $0.6\times 10^{-10}\Omega$ cm when the specimen was heated at 700°C in oxygen under a partial pressure of 7.3×10^{-2}mm Hg. The decrease is probably due to oxidation of the impurities present.

Extrapolating Eq. (25), the equilibrium concentration of oxygen in silver at 700°C under oxygen at a partial pressure of 2.3 mm Hg is 4.7×10^{-6}. This concentration corresponds to a change in the electrical resistivity of $1.0\times 10^{-10}\Omega$ cm. Thus one atomic per cent oxygen in silver gives about $2\times 10^{-6}\Omega$ cm. The oxidized specimen was heated in a vacuum at 700°C for 2 h, and the residual resistivity returned to the original value. This fact indicates that oxygen goes into and out of silver easily upon heating under an oxygen atmosphere because silver oxide is unstable above 400°C.

The concentration of oxygen in M.S.C. helium is less than 5×10^{-6}, which gives a concentration of oxygen in silver less than 10^{-7} at 700°C. This is only 8% of the concentration of vacancies at 700°C.

The activation energy of diffusion of oxygen in silver was measured by Johnson and Larose and determined to be 0.98 eV.[16]

J. Other Quenching Results on Silver

Recently Quéré has published two short papers concerning defects in quenched silver.[17] In many respects his data agree with the present research. There are several important differences for which one can suggest possible reasons.

Quéré quenches 8-mil wires by turning off the current. The wires are heated and quenched in an atmosphere of argon. His quenched-in resistivity obeys the usual equation [i.e., Eq. (1)] with $A=(4.9\pm 1.5)\times 10^{-4}\Omega$ cm and $E_F{}^V=1.06\pm 0.07$ eV. These values are in excellent agreement with ours and with the equilibrium results at the melting point measured by Simmons and Balluffi.[9] But this result is very surprising. The rate of heat conduction in argon is less than one-eighth of that in helium at the same temperature. In the experiments reported here the amount quenched-in is dependent on quenching rate, particularly at high quenching temperatures where some bending is observed even during a 14 msec quench. Unfortunately, Quéré does not report his quenching rates; he states that his results do not depend very critically on the rate of quenching. Quéré uses 8-mil wire whereas the present work was done with 2-mil specimens; thus he has 16 times as much material to cool.

In his second paper Quéré mentions that he anneals for 2 h at 55°C to return to solution those vacancies which are trapped during the quench. He does not indicate how much, if any, of the quenched-in resistivity anneals during this treatment. In the present experiments a very large amount of the quenched-in resistivity would disappear during such an anneal, i.e., about 80%. Apparently his annealing measurements are made after this 2-h treatment.

Quéré does not determine the order of the annealing kinetics nor does he give lifetimes, but one can make rough estimates of the lifetimes from his isothermal annealing curves. For a quench from 760°C and an anneal at 120°C the time for the resistivity to decay to $1/e$ times the original value is about 166 sec, during which time a divacancy will make 3.3×10^{8} atomic jumps if no trapping occurs. In the experiments re-

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ported in the present paper the dislocation densities were such that the number of jumps required to reach a dislocation was 2×10^6, i.e., the divacancy lifetime measured at 90.3°C 4 was sec. Hence, Quéré's divacancy lifetime is long. This could result from trapping at impurities or it is possible that he has fewer dislocations than exist in the two-mil wires. The solubility of oxygen under 2 mm Hg of the partial pressure of oxygen is 4.7×10^{-6} (see Sec. IV, I). It is unfortunate that Quéré does not report the residual resistivity of his well-annealed wires, nor does he quote the amount of resistivity annealing out during his 55°C anneals, nor the resistivity changes which occur during his annealing studies.

Nevertheless the amounts which Ouéré quenches in agree well with Simmons and Balluffi and with the present determination. In addition, his divacancy migration energy agrees with the present results and his vacancy migration energy is also in agreement with the data given here.

K. Relation to the Annealing of Quenched Gold

In conclusion, one can contrast the results obtained on silver with those obtained on gold. In gold, the binding energy of the divacancy is only 0.10 eV so that it is not too difficult to obtain specimens containing only vacancies at room temperature. In silver, the binding energy of the divacancy is considerably larger and it is only by pulsing that one can obtain single vacancies at room temperature in a specimen which has any reasonable total void concentration. Self-diffusion occurs by single vacancy motion in both gold and silver since the high temperatures used are sufficient to break up most divacancies. The annealing kinetics after quenching differ profoundly in the two metals. This difference results mainly from the difference in the divacancy binding energy in the two materials. The binding energies of larger clusters may also have some influence.

V. SUMMARY

(1) The formation energy $E_F{}^V$ of a single vacancy is 1.10 ± 0.04 eV.

(2) The activation energy for motion of a single vacancy is 0.83 ± 0.05 eV.

(3) Conclusions (1) and (2) indicate that diffusion in pure silver occurs mainly by the "vacancy mechanism."

(4) The resistivity increment $\Delta\rho$ (1%) produced if 1% of the lattice sites is vacant is 1.3 ± 0.7 $\mu\,\Omega$ cm; most of the voids are divacancies.

The following conclusions are more tentative:

(5) Most of the quenched-in defects are divacancies. This is consistent with the high binding energy observed between single vacancies. Most of these divacancies are formed during a quench.

(6) The annealing kinetics below 0°C are second order, indicating that divacancies combine to form quadrivacancies.

(7) The activation energy for motion of a divacancy is 0.57 ± 0.03 eV.

(8) Below 0°C two divacancies combine to form a quadrivacancy. The indications are that a quadrivacancy is much less mobile than a single vacancy or a divacancy.

(9) The binding energy B_Q of a quadrivacancy, if it dissociates into two divacancies, is between 0.22 and 0.38 eV.

(10) Near 100°C the half-time is about 4 sec at 90.3°C. In this temperature range a freshly quenched specimen anneals by the motion of divacancies to dislocations.

(11) The binding energy, B_{Di}, of a divacancy relative to dissociation into vacancies is 0.38 ± 0.05 eV.

(12) Above 90°C, the quadrivacancy formed when two divacancies meet is not stable. It breaks up into divacancies in less than 4 sec at 90°C.

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