

Pressure Effect on Vacancy Formation in Gold

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99.999% pure gold wires were resistance heated to 680°C in a gaseous medium at pressures between 400 and 11 000 atmospheres and quenched by turning off the heating current. The temperature decayed exponentially with a half-life of 1.6×10^{-2} sec. The logarithm of the quenched-in electric resistance ΔR decreased linearly with increasing pressure. From the pressure effect on ΔR an activation volume for vacancy formation at 680°C of $\Delta V_f = (9.16 \pm 0.68) \times 10^{-24}$ cm³ = 0.53 ± 0.04 atomic volume is derived, assuming that the quenched-in resistivity is due to the formation of single vacancies. In the pressure range investigated, ΔV_f is apparently independent of the pressure. Using ΔV_f and Bauerle and Koehler's relationship between resistivity and fractional volume change during recovery, the electric resistivity of vacancies is $(1.8 \pm 0.4) \times 10^{-6}$ Ω cm/at. % and the vacancy concentration after quenching from 680°C at room pressure with 1.6×10^{-2} sec half-life of the temperature decay is $(2.4 \pm 0.5) \times 10^{-8}$. The present data are in good agreement with those reported by DeSorbo from a calorimetric study of quenched foil. The present defect concentration is about 50% of the value extrapolated to 680°C from the data of Simmons and Balluffi, who obtained the vacancy concentration in thermal equilibrium near the melting temperature.

I. INTRODUCTION

IN a crystal, a large number of structural defects is in thermal equilibrium with the perfect lattice at high temperatures. In face-centered cubic metals, vacancies are favored as the defects rather than interstitial atoms, because they require an activation energy of formation of about one-third of the energy necessary to form interstitial atoms.¹ By rapid quenching of a metal from a high temperature, a large number of vacancies, which is in thermal equilibrium with the perfect lattice at the high temperature, is frozen within the lattice. The quenching technique has been used frequently to study the physical properties of vacancies in metals.

Most of the experimental work on pure metals has been done with gold. In gold the effect of quenching and annealing on the electric resistivity,²⁻⁷ the macroscopic length,^{4,8} the energy stored in the lattice,^{9,10} the yield stress,⁷ the internal friction,¹¹ and the electron microscopic transmission^{6,12} has been investigated. The effect of the heating-time¹³ and the quench rate^{4,14} on the

quenched-in resistivity and the influence of pressure¹⁵ and plastic deformation^{16,17} on the annealing rate of the quenched-in resistivity has also been studied.

The physical properties of the lattice vacancy can be derived from an investigation of a quenched specimen only if the vacancy concentration is known. Strictly empirical information on the vacancy concentration in gold has been given by several authors. The work, which is reported, includes the measurement of the total energy released by annealing of quenched specimens together with the activation energy of vacancy formation,^{9,10} the investigation of the macroscopic length expansion and the change in the lattice parameter of a heated specimen under thermal equilibrium conditions,¹⁸ and the measurement of the concentration and the size of the stacking fault tetrahedra formed by vacancy condensation in quenched and annealed foils.⁶ However, the results of the different authors differ by nearly an order of magnitude. Therefore, further information on fundamental vacancy properties is desirable.

A fundamental property of the lattice vacancy, which also leads to an empirical determination of the defect concentration, is the activation volume of formation together with the fractional length change due to the quenched-in defects. The activation volume of formation can be determined by measuring the pressure effect on the relative vacancy concentration in quenched specimens.¹⁹ The formation of divacancies and higher order clusters increases with increasing quench temperature. However, theoretical analyses²⁰⁻²² of the

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¹ The first theoretical study of the activation energy of formation of vacancies and interstitials in close-packed metals has been reported by H. B. Huntington and F. Seitz, *Phys. Rev.* **61**, 315 (1942). References regarding the numerous recent theoretical work on point defects in metals may be obtained from R. A. Johnson and E. Brown, *Phys. Rev.* **127**, 446 (1962).

² J. W. Kauffman and J. S. Koehler, *Phys. Rev.* **88**, 149 (1952); **97**, 555 (1955).

³ F. J. Bradshaw and S. Pearson, *Phil. Mag.* **2**, 379 (1957).

⁴ J. E. Bauerle and J. S. Koehler, *Phys. Rev.* **107**, 1493 (1957).

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

⁶ R. M. J. Cotterill, *Phil. Mag.* **6**, 1351 (1961).

⁷ T. Mori, M. Meshii, and J. W. Kauffman, *Acta Met.* **9**, 71 (1961).

⁸ J. Takamura, *Acta Met.* **9**, 547 (1961).

⁹ W. DeSorbo, *Phys. Rev.* **117**, 444 (1960).

¹⁰ V. A. Pervakov and V. I. Khotkevich, *Doklady Akad. Nauk. S.S.S.R.* **134**, 1328 (1960) [translation: *Soviet Phys.—Doklady* **5**, 1051 (1961)].

¹¹ R. Kamel, *Acta Met.* **7**, 680 (1959).

¹² J. Silcox and P. B. Hirsch, *Phil. Mag.* **4**, 72 (1959).

¹³ J. J. Jackson and J. S. Koehler, *Bull. Am. Phys. Soc.* **5**, 154 (1960).

¹⁴ T. Mori, J. W. Kauffman, and M. Meshii, *Bull. Am. Phys. Soc.* **6**, 157 (1961).

¹⁵ R. M. Emrick, *Phys. Rev.* **122**, 1720 (1961).

¹⁶ M. Meshii and J. W. Kauffman, *Acta Met.* **8**, 815 (1960).

¹⁷ S. Yoshida and J. S. Koehler, *Acta Met.* **8**, 878 (1960).

¹⁸ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **125**, 862 (1962).

¹⁹ R. C. Lowell and C. T. Tomizuka, *Bull. Am. Phys. Soc.* **5**, 182 (1960).

²⁰ J. S. Koehler, F. Seitz, and J. E. Bauerle, *Phys. Rev.* **107**, 1499 (1957).

²¹ H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, *Acta Met.* **7**, 145 (1959).

²² G. Schottky, *Z. Physik* **160**, 16 (1960).

earlier quench experiments have shown that, for quench temperatures less than 700°C and for quench rates in the order of 10^4 °C/sec, the concentration of vacancy clusters is apparently negligible.

In the present investigation 99.999% pure gold wires were resistance heated to 680°C in a gaseous medium within a high-pressure cell at different pressure levels and quenched by turning off the heating current. The temperature decayed exponentially with a half-life of 1.6×10^{-2} sec. From the change of the quenched-in electrical resistance with the pressure the activation volume of formation of vacancies is derived. Using the proportionality constant between the resistivity changes and the fractional-length changes during annealing of quenched gold wires, measured by Bauerle and Koehler,⁴ the electric resistivity per atomic percent vacancies and the quenched-in vacancy concentration is determined.

II. THEORY

The change of the Gibbs free energy due to formation of n lattice vacancies in a perfect crystal containing N similar atoms under the assumption

$$n \ll N \quad (1)$$

is at constant pressure p and constant temperature T

$$\Delta G_f(n, p, T) = n\Delta U_f + n p \Delta V_f - n T \Delta S_{th} - k T \ln \frac{N!}{n!(N-n)!}. \quad (2)$$

ΔU_f , ΔV_f , and ΔS_{th} are the change per vacancy of the internal energy, the volume, and the thermal entropy of the crystal, respectively, k is Boltzmann's constant. We find the equilibrium vacancy concentration c from Eq. (2) using the equilibrium condition

$$\left(\frac{\partial \Delta G_f}{\partial n}\right)_{p, T} = 0, \quad (3)$$

and employing the Stirling formula in the form $\ln x! = x \ln x$ for $x \gg 1$:

$$c(p, T) = n(p, T)/N = e^{\Delta S_{th}/k} e^{-(\Delta U_f + p \Delta V_f)/kT}. \quad (4)$$

According to Eq. (4) the change of the vacancy concentration with pressure is given by

$$\frac{\partial \ln c}{\partial p} = -\frac{1}{kT} \left(-T \frac{\partial \Delta S_{th}}{\partial p} + \frac{\partial \Delta U_f}{\partial p} + p \frac{\partial \Delta V_f}{\partial p} + \Delta V_f \right). \quad (5)$$

Under the assumption, that the first two terms on the right hand of Eq. (5) are small compared to ΔV_f , we can approximate Eq. (5) by

$$\frac{\partial \ln c}{\partial p} = -\frac{1}{kT} \left(p \frac{\partial \Delta V_f}{\partial p} + \Delta V_f \right). \quad (6)$$

As will be shown by the present experimental results, the logarithmic derivative of the vacancy concentration with respect to pressure is independent of the pressure

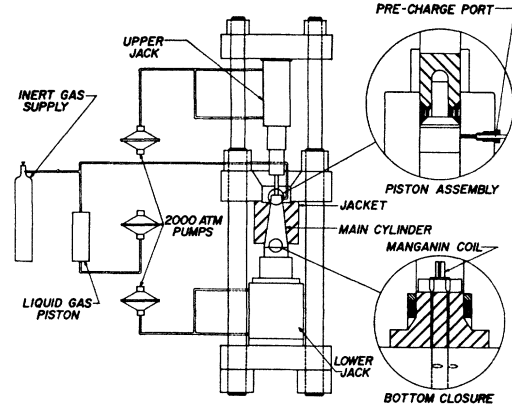


FIG. 1. The high-pressure system.

within the pressure range studied. This indicates that

$$p \frac{\partial \Delta V_f}{\partial p} \ll \Delta V_f. \quad (7)$$

Equation (6) then becomes

$$\frac{\partial \ln c}{\partial p} = -\Delta V_f / kT. \quad (8)$$

From Eq. (8) we find

$$c(p, T) = c(p_0, T) e^{-\Delta V_f (p - p_0) / kT}. \quad (9)$$

According to Eq. (8) the activation volume of formation of lattice vacancies is given by the logarithmic derivative of the vacancy concentration with respect to the pressure. We assume that at the quench-temperature of 680°C only single vacancies are formed. The relative change of the vacancy concentration with the pressure can be determined by the measurement of the pressure effect on the quenched-in electrical resistance, assuming a linear proportionality between the single vacancy concentration and the quenched-in resistance.

III. PRESSURE SYSTEM

The hydrostatic pressure system²³ used in this investigation is shown in Fig. 1. The system operates by precharging the main cylinder to a pressure of approximately 2000 atm, using a precharge pump and a liquid-gas piston. The pressure is further increased by driving the piston into the cylinder using the upper jack as shown in Fig. 1. As the piston moves, it passes the precharge port, thus preventing extreme pressures from entering the precharge system. The piston, which is shown in Fig. 1, is of the unsupported area type. It is sealed against the cylinder wall using gaskets made of Teflon and rubber between two brass wedge rings. Gaskets made of copper and lead between two wedge rings of Monel are used to seal the bottom closure. In order to compensate for the internal pressure inside the main cylinder, the cylinder is forced simultaneously with

²³ The high-pressure system is manufactured by the Harwood Engineering Company, Walpole, Massachusetts. It is similar to the type used by Birch *et al.* [F. Birch, E. C. Robertson, and S. P. Clark, *Ind. Eng. Chem.* **49**, 1965 (1957)].

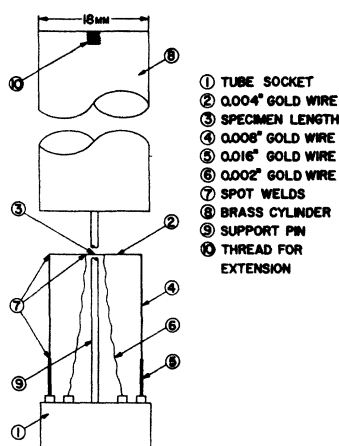


FIG. 2. Sketch of the specimen holder.

the increase in pressure into a tapered jacket by means of the lower jack. With this arrangement, the system has a capacity of 12 000 atm.

The pressure cell has an inside diameter of 19 mm and a length of 100 mm after the full stroke of the piston. Approximately 80% of this space is additionally filled with a brass cylinder to increase the compression ratio of the device. The pressure is measured by its effect on the electrical resistivity of a manganin coil. The manganin coil, which has a resistance of about 120 Ω , is mounted on the bottom closure inside the main cylinder. It was calibrated against a controlled clearance free piston gauge and was found to be linear within $\pm 1.5\%$ between 0 and 10 000 atm. The leads of the manganin coil and the several leads, which are connected with the sample inside the pressure cell, enter the main cylinder through the bottom closure.

IV. EXPERIMENTAL PROCEDURE

The specimen material is polycrystalline 99.999% pure gold wire of 0.004-in. diam.²⁴ The specimen is mounted on a tube socket which fits on a series of pins connected with the electrical leads in the bottom closure of the pressure cell (Fig. 2). To keep stresses, induced by the support, as small as possible, the specimen is spot-welded to a 0.008-in.-diam gold wire, which is connected with the tube socket by a short length of 0.016-in.-diam gold wire. Potential leads of 0.002-in.-diam gold wire are spot-welded to the central part of the specimen wire. The specimen length between the potential leads is about 3 mm and the over-all length of the specimen wire is 15 mm. All gold wires used in mounting of the specimen are 99.999% pure.²⁴ The sample holder can be inserted into the pressure cell, after removal of the piston, by an extension screwed into the specimen holder. The specimen is heated by passing dc current

²⁴ Obtained from the Sigmund Cohn Corporation, Mount Vernon, New York. According to a qualitative spectrographic analysis obtained from the supplier, traces of silver, copper, and lead of less than 0.001% total have been found in the bar used for the specimen wire. No other metals were found.

through it. The temperature of the specimen is measured by determining its electrical resistance. The uniformity of the temperature over the specimen length was checked in a helium atmosphere at room pressure using a moving potential lead in combination with a micrometer microscope. The moving potential lead is a nichrome strip of 0.002-in. thickness and 0.004-in. width, which is slightly touching the specimen wire. In Fig. 3, the relative voltage drop per fractional length is plotted vs the fractional length of the specimen. As shown in Fig. 3, the measurements indicated a temperature uniformity over the specimen length at 685°C within $\pm 10^\circ\text{C}$.

After mounting, the specimen is annealed in nitrogen at room pressure at 850°C for 100 min and at 600°C for 5 min. Before each pressure run, the specimen is heated in nitrogen at room pressure to 850°C for 5 min and to 600°C for 5 min and cooled to room temperature within about 10 min. The sample holder is then inserted into the high-pressure cell. After the desired pressure is built up, the room-temperature electrical resistance of the specimen is measured. The specimen is then heated to the desired temperature. The temperature is derived from the ratio of the electrical resistance at high temperature and at room temperature measured at the elevated pressure in combination with a resistance-temperature calibration, carried out at room pressure. The pressure effect on the temperature coefficient of the electrical resistivity of gold has been reported between 0° and 100°C in the pressure range 0–12 000 atm.²⁵ According to these data the ratio of the electrical resistivity of gold at 0°C and at 100°C increases by 0.053% due to a pressure of 10 000 atm. Therefore, the pressure effect on the temperature coefficient of the electrical re-

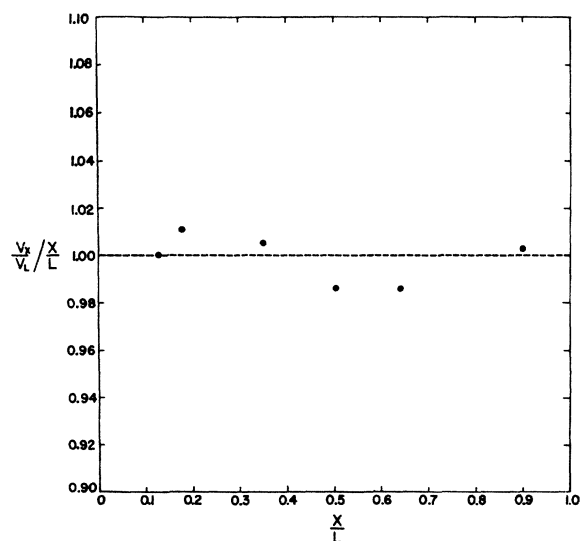


FIG. 3. Relative voltage drop per fractional length of the wire vs the fractional length at a temperature of about 685°C in a helium atmosphere at room pressure. The length L is 3.5 mm.

²⁵ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 6, p. 137.

sistivity of the specimen can be neglected, assuming that the effect does not change drastically between 100 and 700°C. The resistance measurements indicated small temperature fluctuations of the specimen in the pressure cell with time. At about 680°C and at pressures in the order of 500 atm, the resistance fluctuations over a period of several minutes corresponded to a temperature fluctuation within $\pm 15^\circ\text{C}$. At higher pressures the amplitude of the fluctuations decreased with increasing pressure. Apparently the fluctuations were caused by convection currents in the highly pressurized gas. The actual quench temperature is measured using a Honeywell Model 906B multichannel recording oscillograph connected with the potential leads of the specimen. The heating current, which also passes through a resistance standard, is measured simultaneously with the voltage drop across the specimen using a second channel of the oscillograph. Only those quench runs were analyzed in which the oscillograph indicated that the quench temperature was constant within $\pm 7^\circ\text{C}$ during a time of 0.25 sec immediately before quenching. The time dependence of the appearance of the quenched-in electrical resistance has been reported using pulse-heated gold wires¹³; it was found that at 650°C a time of 0.08 sec is required to produce half the equilibrium resistance increment. Data reported^{4,14} on the influence of the quenching rate on the quenched-in resistivity in gold indicate also that during a small temperature drop at about 700°C the vacancy concentration reaches the new equilibrium value after a half-life which is not larger than 0.08 sec. Therefore, we can derive from our oscillographic temperature readings that the equilibrium value of the vacancy concentration was reached in all samples with an uncertainty of the quench temperature of $\pm 7^\circ\text{C}$.

Quenching is performed by abruptly dropping the heating current from 8–11 A to 0.2 A. Simultaneously the sensitivity of the oscillograph is increased. After dropping the heating current, the potential drop across the specimen decreased exponentially with a half-life of about 1.6×10^{-2} sec, indicating an initial quench-rate of larger than about 2×10^4 °C/sec. The quench rate depends on the gas, used as the pressure medium and also on the pressure, since the thermal conductivity of gases is slightly pressure dependent in the pressure range investigated.²⁶ At quench rates in the order of 2×10^4 °C/sec the quenched-in resistance increases slightly with increasing quench rate.^{4,14} In order to obtain the same quench rate at all pressure levels, different gases were used at different pressures. The experiments were carried out using helium, nitrogen, and argon.^{26a} Immediately after quenching to room temperature, the

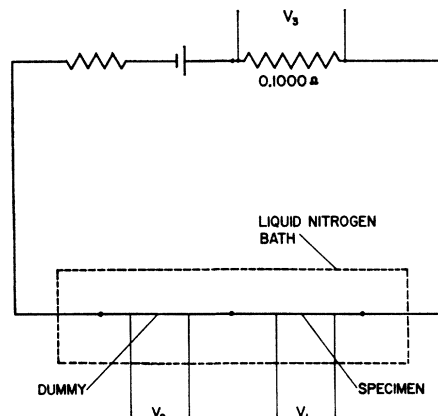


FIG. 4. Schematic of the electric resistance measurements.

signal current is turned off and the pressure is released within 30 min. Approximately 60 min after quenching the sample is immersed into liquid nitrogen.

After immersing the specimen into liquid nitrogen, the electrical resistance is measured following the scheme as shown in Fig. 4. A current of about 300 mA passes through the specimen and through a 0.1000-Ω resistance standard, which is kept at room temperature. Temperature changes of the liquid nitrogen bath during the experiment are detected by taking the resistance value of an annealed dummy specimen which is continuously kept in the low temperature bath in series with the sample. To reduce temperature fluctuations due to convection currents in the liquid nitrogen, the specimen and the dummy are each inserted into a closely fitting perforated copper cylinder before immersing into the low-temperature bath. The voltages V_1 , V_2 , and V_3 , indicated in Fig. 4, are measured with a Rubicon Model 2768 microvolt potentiometer in combination with a Keithley Model 149 millimicrovolt meter. The voltage triplet, V_1 , V_2 , and V_3 , is read several times in the same sequence. The potential leads connected with the specimen and the dummy consist of 99.999% pure gold wires to reduce thermoelectric effects. The thermoelectric voltage within the sample and the dummy was less than 0.2 μV . The relative error due to thermal emf's within the 0.1-Ω resistance standard was less than 10^{-6} . The error due to thermoelectric effects within the circuitry is compensated by reversing the current.

After the resistance measurement, the quenched specimen is heated for 5 min to 800°C and for 100 min to 400°C in nitrogen at room pressure and then cooled to room temperature within several minutes. The electrical resistance of the annealed specimen is measured after each quench run carried out at elevated pressures. A typical set of data is shown in Table I. The resistance of the quenched specimen is given by

$$R_q = (V_1/V_3)_q \times 0.1000 \Omega; \quad (10)$$

the resistance of the annealed specimen is calculated

²⁶ S. D. Hamann, *Physico-Chemical Effects of Pressure* (Butterworths Scientific Publications, Ltd., London, 1957), p. 90.

^{26a} The following impurities are specified by the supplier as typical contaminants of the gases: for helium and argon: $\text{N}_2 < 50$ ppm, $\text{H}_2 < 5$ ppm, $\text{O}_2 < 5$ ppm, $\text{H}_2\text{O} < 3$ ppm, hydrocarbons < 15 ppm; for nitrogen: 0.1% H_2O , 0.09% O_2 , 0.1–0.2% noble gases.

TABLE I. Measured values of the voltage ratio V_1/V_3 and V_2/V_3 of a specimen after quenching and after annealing using the scheme as shown in Fig. 4.

| | | $(V_1/V_3) \times 10^3$ | $(V_2/V_3) \times 10^3$ |
|-------------------|-----------------|-------------------------|-------------------------|
| Quenched specimen | Forward current | 8.9379 ± 0.0019 | 25.659 ± 0.007 |
| | Reverse current | 8.9367 ± 0.0008 | 25.655 ± 0.001 |
| | Average value | 8.9373 ± 0.0019 | 25.657 ± 0.007 |
| Annealed specimen | Forward current | 8.7813 ± 0.0012 | 25.663 ± 0.003 |
| | Reverse current | 8.7836 ± 0.0018 | 25.651 ± 0.001 |
| | Average value | 8.7825 ± 0.0018 | 25.657 ± 0.003 |

using the equation

$$R_a = (V_1/V_3)_a \times (V_3/V_2)_a \times (V_2/V_3)_q \times 0.1000 \Omega. \quad (11)$$

The subscripts q and a refer to the quenched and the annealed specimen, respectively. The correction factor $(V_3/V_2)_a \times (V_2/V_3)_q$ compensates for a temperature change in the liquid nitrogen bath between the measurements carried out with the quenched and with the annealed specimen. Using the average values given in Table I in connection with Eqs. (10) and (11) we find $R_q = (8.9373 \pm 0.0019) \times 10^{-4} \Omega$, $R_a = (8.7825 \pm 0.0018) \times 10^{-4} \Omega$, with a quenched-in resistance of $\Delta R = (1.548 \pm 0.037) \times 10^{-5} \Omega$.

V. RESULTS

To check the experimental procedure, the dependence of the quenched-in resistance on the quench temperature was studied at a pressure of 1800 atm. From the data shown in Fig. 5, we derive the activation energy for vacancy formation in gold

$$\Delta H_f = \Delta U_f + p\Delta V_f = 0.98 \text{ eV}, \quad (12)$$

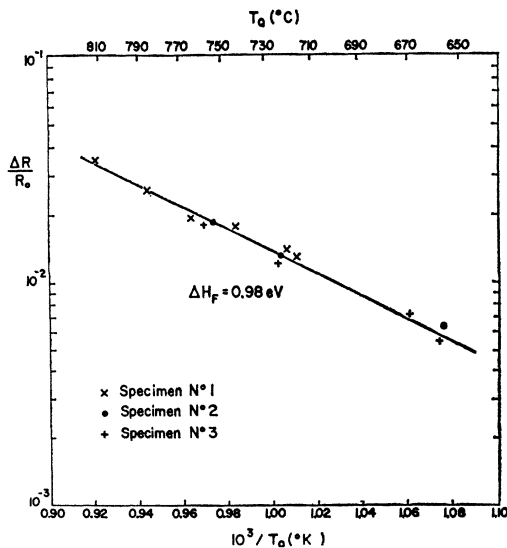


FIG. 5. Semilogarithmic plot of the relative resistance quenched in at 1800 atm vs reciprocal of the absolute quench temperature. R_0 is the annealed resistance at the temperature of liquid nitrogen.

which is in good agreement with the value reported at room pressure.^{3,4,8,9,15,18} Specimens No. 1 and No. 2 of Fig. 5 were quenched in a helium atmosphere with a half-life of the temperature decay within $(1.20 \pm 0.06) \times 10^{-2}$ sec. The specimen No. 3 of Fig. 5 was quenched in a nitrogen atmosphere with a half-life of the temperature decay within $(2.02 \pm 0.06) \times 10^{-2}$ sec.

The studies of the pressure effect on the quenched-in resistance are summarized in Table II. The half-life of the temperature decay in all quench runs, shown in Table II, was $(1.57 \pm 0.13) \times 10^{-2}$ sec. Because of the temperature fluctuations of the heated specimen in the pressure cell, it was difficult to reproduce the quench temperature exactly. The error in the quench temperature T_q , indicated in column 4 of Table II, is given by the deviation from the average quench temperature within 0.25 sec immediately before quenching. The measured values of the relative resistance increment, given in column 5 of Table II, were extrapolated to a quench temperature of 680°C, using an Arrhenius-type equation. An activation energy of 0.98 eV was used to correct for the quench temperature at all pressure levels. It can be estimated, using an activation volume for vacancy formation of 0.5 atomic volume (at. vol.), that the pressure effect on ΔH_f introduces a negligible influence on the temperature correction. As shown in Fig. 6, the logarithm of the quenched-in electrical resistance, corrected for $T_q = 680^\circ\text{C}$, decreases linearly with increasing pressure. This indicates the validity of the relation (7). The straight line with the least-squares fit, drawn through the points in Fig. 6, corresponds to the activation volume for vacancy formation in gold

$$\Delta V_f = (9.16 \pm 0.68) \times 10^{-24} \text{ cm}^3 \quad (13)$$

following Eq. (8). Using the molar volume of gold at room temperature of 10.2 cm³/mole and the thermal volume expansion at 680°C of 3.2%²⁷ and neglecting the pressure effect on the density of gold because of the

TABLE II. Summary of the data for the different pressure levels. $\Delta R/R_0$ is the relative resistance quenched in from T_q given in column 4. $(\Delta R/R_0)$ corr. is the value of column 5 corrected for $T_q = 680^\circ\text{C}$. R_0 is the resistance of the specimen at the temperature of liquid nitrogen.

| Specimen No. | p (10 ³ atm) | Pressure medium | T_q (°C) | $(\Delta R/R_0)$ ($\times 10^3$) | $(\Delta R/R_0)$ corr. ($\times 10^3$) |
|--------------|---------------------------|-----------------|------------|------------------------------------|--|
| 4 | 11.0 | N ₂ | 689 ± 0 | 4.57 | 4.06 |
| 5 | 0.42 | He | 681 ± 4 | 9.50 | 9.36 |
| 6 | 5.0 | N ₂ | 677 ± 7 | 6.41 | 6.60 |
| 6 | 8.08 | N ₂ | 693 ± 3 | 5.92 | 5.02 |
| 7 | 5.0 | N ₂ | 656 ± 4 | 4.37 | 5.93 |
| 8 | 0.70 | He | 678 ± 7 | 7.81 | 7.98 |
| 8 | 3.1 | N ₂ | 672 ± 7 | 7.07 | 7.80 |
| 8 | 5.0 | N ₂ | 699 ± 3 | 7.86 | 6.21 |
| 8 | 8.0 | N ₂ | 678 ± 4 | 5.07 | 5.17 |
| 8 | 10.1 | Ar | 678 ± 0 | 4.63 | 4.71 |

²⁷ Handbook of Thermophysical Properties of Solid Materials (Pergamon Press, New York, 1961), Vol. 1.

small compressibility,²⁸ the molar volume at 680°C is 10.5 cm³/mole. With this value the activation volume, given in Eq. (13), corresponds to

$$\Delta V_f = 0.53 \pm 0.04 \text{ at. vol.} \quad (14)$$

Bauerle and Koehler⁴ measured the relative length contraction at 30°C concurrently with the resistance decay of quenched gold wires during annealing. Assuming that the dimensional changes are isotropic and of the same value due to either vacancy formation or vacancy annihilation, the results of these authors indicate the proportionality constant between the resistivity change $\Delta\rho$ and the fractional volume change $\Delta V/V$ due to vacancy formation²⁹

$$\Delta\rho/(\Delta V/V) = (3.4 \pm 0.5) \times 10^{-4} \Omega \text{ cm.} \quad (15)$$

The relative volume change due to formation of n lattice vacancies in a crystal containing N similar atoms is given by

$$\Delta V/V = n\Delta V_f/N\mathcal{V}, \quad (16)$$

where \mathcal{V} is the atomic volume of the atoms in the crystal. Using Eqs. (15) and (16) and the value of $\Delta V_f/\mathcal{V}$ given in (14), we have

$$\Delta\rho/(n/N) = (1.8 \pm 0.4) \times 10^{-6} \Omega \text{ cm/at.}\% \quad (17)$$

With the relative resistance increment extrapolated to room pressure according to Fig. 6, the resistivity of the specimen at liquid-nitrogen temperature of $0.470 \times 10^{-6} \Omega \text{ cm}$ and the resistivity per atomic percent vacancies given in Eq. (17), the vacancy concentration after quenching at room pressure from a temperature of 680°C, which decays exponentially with a half-life of $1.6 \times 10^{-2} \text{ sec}$, is

$$n/N = (2.4 \pm 0.5) \times 10^{-5}. \quad (18)$$

VI. DISCUSSION

A. Activation Volume of Formation

The value of ΔV_f , given in Eq. (14), is in good agreement with the value $0.57 \pm 0.05 \text{ at. vol.}$, reported by DeSorbo,⁹ who derived ΔV_f indirectly from the total energy released by annealing of quenched gold foils, the activation energy of vacancy formation and the value of $\Delta\rho/(\Delta V/V) = 3.2 \times 10^{-4} \Omega \text{ cm}$ taken from the experiments of Bauerle and Koehler.⁴ Simmons and Balluffi¹⁸ found $\Delta V_f = 0.45 \pm 0.10 \text{ at. vol.}$ These authors measured the vacancy concentration under equilibrium conditions by studying concurrently the macroscopic length and the lattice parameter of a heated specimen. They derived ΔV_f from their value of the equilibrium

²⁸ P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1952), p. 161.

²⁹ This value is given as the best interpretation of the experimental evidence according to C. P. Flynn, *Phys. Rev.* **125**, 881 (1962).

vacancy concentration in combination with Bauerle and Koehler's⁴ fractional length measurements of quenched wires. Since Simmons and Balluffi neglected the fact that in Bauerle and Koehler's experiments vacancies were lost during quenching, their average value of ΔV_f is apparently slightly too small.

The present result is in good agreement with the recent theoretical work of Johnson and Brown,¹ Tewordt³⁰ and Bennemann,³¹ made for copper. The different authors found a value of $\Delta V_f/\mathcal{V}$ of 0.52, 0.47 to 0.55, and 0.60, respectively. Seeger and Mann³² calculated a value of $\Delta V_f/\mathcal{V}$ in copper of 0.7 to 0.8.

From an investigation of the pressure effect on the annealing rate of vacancies quenched into gold wires, Emrick¹⁵ has derived an activation volume of motion of $\Delta V_m/\mathcal{V} = 0.15 \pm 0.014$. With the present result the activation volume for self-diffusion in gold, assuming the vacancy mechanism, is then given as $(\Delta V_f + \Delta V_m)/\mathcal{V} = 0.68 \pm 0.05$. This value compares favorably with the value 0.7 reported for lead^{33,34} and is slightly smaller than the value 0.90 reported for silver.³⁵

B. Monovacancy Resistivity

The value of $\Delta\rho/(n/N)$ given in Eq. (17) is in good agreement with the value $\Delta\rho/(n/N) = (1.8 \pm 0.6) \times 10^{-6} \Omega \text{ cm/at.}\%$ reported by DeSorbo⁹ from his calorimetric work in combination with the resistivity data of Bauerle and Koehler.⁴ Simmons and Balluffi¹⁸ found $\Delta\rho/(n/N) = (1.5 \pm 0.3) \times 10^{-6} \Omega \text{ cm/at.}\%$ using their value of the equilibrium vacancy concentration together with Bauerle and Koehler's resistivity data. Their average value of $\Delta\rho/(n/N)$ is probably slightly too small, since

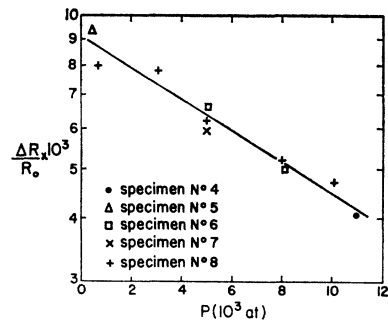


FIG. 6. Semilogarithmic plot of the relative resistance quenched in at 680°C vs the gas pressure during quenching. The data are extrapolated from column 5 of Table II to the quench temperature of 680°C using an Arrhenius-type equation with an activation energy of 0.98 eV. R_0 is the annealed resistance at the temperature of liquid nitrogen.

³⁰ L. Tewordt, *Phys. Rev.* **109**, 61 (1958).

³¹ K. H. Bennemann, *Z. Physik* **165**, 445 (1961).

³² A. Seeger and E. Mann, *J. Phys. Chem. Solids* **12**, 326 (1960).

³³ N. H. Nachtrieb, H. A. Resing, and S. A. Rice, *J. Chem. Phys.* **31**, 135 (1959).

³⁴ J. B. Hudson, in *Progress in Very High Pressure Research*, edited by F. Bundy, W. R. Hibbard, and H. M. Strong (John Wiley & Sons, Inc., New York, 1961), p. 269.

³⁵ C. T. Tomizuka, in *Progress in Very High Pressure Research*, edited by F. Bundy, W. R. Hibbard, and H. M. Strong (John Wiley & Sons, Inc., New York, 1961), p. 266.

TABLE III. Summary of the reported experimental data on the activation volume of formation, $\Delta V_f/v$, the electrical resistivity per atomic percent, $\Delta\rho/(n/N)$, and the concentration at room pressure, n/N , of monovacancies in gold.

| Authors | $\Delta V_f/v$ | $\Delta\rho/(n/N)$ | $(n/N)(\times 10^6)$ | |
|---|-----------------|--|----------------------|---------------|
| | | ($\times 10^6$) ($\Omega\text{cm/at.}\%$) | 890°C | 680°C |
| Cotterill ^a | ... | 2.4 ± 0.4 | 12 ± 4 | ... |
| DeSorbo ^b | 0.57 ± 0.05 | 1.8 ± 0.6 | 12.4 | 2.4^c |
| Pervakov and Khotkevich ^d | ... | 0.30 | 76 ± 10 | ... |
| Simmons and Balluffi ^e | 0.45 ± 0.10 | 1.5 ± 0.3 | 22 | 4.7^e |
| Present work | 0.53 ± 0.04 | 1.8 ± 0.4 | ... | 2.4 ± 0.5 |

^a See reference 6.

^b See reference 9.

^c Extrapolated value.

^d See reference 10.

^e See reference 18.

they neglected the vacancy losses during quenching in the experiments of Bauerle and Koehler.

Cotterill⁶ reported the value $\Delta\rho/(n/N) = (2.4 \pm 0.4) \times 10^{-6} \Omega \text{ cm/at.}\%$. This author measured the change in the electrical resistivity of gold foils due to quenching and correlated the results with concentration counts obtained by transmission electron microscopy after annealing of the specimens. Since the concentration counts detected only those vacancies which are condensed in the form of tetrahedra of stacking faults and neglected those defects which are lost at grain boundaries or dislocations during annealing, Cotterill's average value of $\Delta\rho/(n/N)$ is probably too large. Pervakov and Khotkevich¹⁰ reported potentiometric measurements of the electrical resistance at 20°C in parallel with calorimetric measurements with quenched and annealed wires. They found $\Delta\rho/(n/N) = 0.30 \times 10^{-6} \Omega \text{ cm/at.}\%$. For a quench temperature of 890°C they measured a resistance increment of 1% of the resistance at 20°C, which corresponds to the value found by several authors using quench rates in the order of 3×10^4 °C/sec. However, the defect concentration, which they derived from their calorimetric data, is larger by a factor of 6 than the value found by DeSorbo.⁹

The value of the vacancy resistivity, given in Eq. (17)

is in good agreement with published theoretical estimates carried out for copper and gold.³⁶

C. Vacancy Concentration

The vacancy concentration n/N , derived by extrapolation of DeSorbo's⁹ n/N data to 680°C with an Arrhenius-type equation, is 2.4×10^{-5} , which is in good agreement with the value given in Eq. (18). Extrapolating the n/N data of Simmons and Balluffi¹⁸ to 680°C, using an Arrhenius-type equation, the value of n/N is 4.7×10^{-5} . The difference between this value, which is obtained under equilibrium conditions, and the value given in Eq. (18) is probably caused by the vacancy losses during quenching of the specimen.

The n/N data obtained by Cotterill⁶ from the electron microscopic concentration counts previously mentioned agree, at quench temperatures below 900°C, approximately with DeSorbo's results and have an error of about $\pm 35\%$. However, the quench rates in Cotterill's experiments are 5 times larger than those reported by DeSorbo. This also indicates that Cotterill's n/N values, which should be higher than DeSorbo's due to the greater quench rate, are probably too small because of the vacancy loss at dislocations and grain boundaries during annealing. As mentioned in Sec. VI B, the n/N value derived by Pervakov and Khotkevich¹⁰ is larger by a factor of 6 than the defect concentration found by DeSorbo.

The reported experimental data on the activation volume of formation, the electrical resistivity and the concentration of monovacancies in gold are summarized in Table III.

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³⁶ The theoretical work on the vacancy resistivity may be obtained from F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 4, p. 199.