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Quenched-in Lattice Defects in Gold*

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High-purity gold wires of 16- and 30-mil diameters were heated to temperatures in the range from 450°C to 1000°C and then quenched to room temperature in water. The time required for the cooling was between 10 and 50 milliseconds. An increase in the residual resistivity was observed which could be described by the equation $\Delta\rho = A e^{-E_F/KT_Q}$. Here $\Delta\rho$ is the extra resistivity, A is a constant equal to $(4.9\pm1.0)\times10^{-4}$ ohm cm, E_F is an energy of formation equal to 0.98 ± 0.03 ev, K is Boltzmann's constant, and T_Q is the temperature from which the quench was made. The resistivity increase annealed in the neighborhood of 40°C with an activation energy for motion ranging from 0.82 ± 0.05 ev for a quench from 700°C to 0.60 ± 0.04 ev for a quench from 1000°C. The annealing kinetics were first order for quenches from 700°C and below but were more complex for quenches from above this temperature. The "half-anneal" times at 40°C ranged from 140 hr for a quench from 700°C to $\frac{1}{2}$ hr for a quench from 1000°C. During the anneals a decrease in specimen length was observed which was at all times proportional to the decrease of the extra resistivity, both for the quenches having first-order annealing kinetics and those having the more complicated annealing behavior. The proportionality constant between the resistivity changes and the fractional-length changes was about 1.1×10^{-3} ohm cm.

I. INTRODUCTION

THE rapid quenching of a close-packed metal from a high temperature should "freeze in" large numbers of lattice vacancies (singles and possibly pairs) which are in thermal equilibrium at the high temperature. In close-packed metals vacancies are favored as the defects rather than interstitial atoms, because they require for formation only about one-third as much energy as interstitials.[1–3] The relative concentration of vacancies present after quenching may be obtained by measuring the increase in electrical resistivity which the vacancies produce. Previous work of this type on pure metals is not plentiful, and for gold the results are somewhat contradictory.[4–6] For these basic studies it would be desirable (1) to extend the range of defect concentrations quenched in, (2) to do a more extensive study of the defect annealing as a function of time and initial concentration, (3) to determine energies of formation and motion for the defects from these data, and (4) to apply simultaneous resistivity and volume-change techniques to some of the annealing studies. Such information should lead to a better understanding of the defects and their annealing mechanisms, and would eventually aid in the interpretation of data obtained in diffusion, in irradiation damage, and in plastic deformation.

In this investigation wires of pure gold were heated to a high temperature and then quenched in water. Gold was chosen because the results could then be compared with existing data and theory, and because it resisted contamination at high temperatures in the presence of water vapor. Water was chosen for the quenching medium because it gave a rapid, reproducible quench and because it produced very little deformation.

II. EXPERIMENTAL PROCEDURE

Specimen material for the experiment was 99.999% pure gold wire of 0.016- and 0.030-inch diameter.[7] After a ten-minute anneal in air (or helium) at 900°C, the ratio of resistance at 4.2°K to that at room temperature was found to be less than 7×10^{-4}, which was consistent with purity quoted. The specimen and a symmetrically arranged dummy were mounted in a light frame as shown in Fig. 1.

Heating of the specimen was accomplished by passing 10–15 amperes of dc through it. The temperature of the specimen gauge length, i.e., the central 4 cm of a 16-cm length, was measured by determining its resistance. Optical pyrometer measurements indicated a temperature uniformity of ±1% over the gauge length.

The quenching process itself was rather simple. As shown in Fig. 2, the specimen frame was supported over water in a partially filled glass tank by three current lead-in wires at one end and a movable stirrup at the other end. Shielding from drafts was provided by the

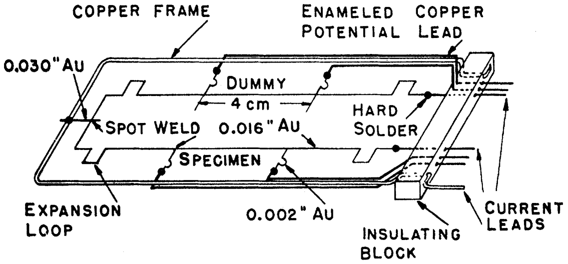

FIG. 1. Details of frame used to hold 16-mil gold specimens for quenching, annealing, and measurement.

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[1] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

[2] H. B. Huntington and F. Seitz, Phys. Rev. **61**, 315 (1942); H. B. Huntington, Phys. Rev. **61**, 325 (1942).

[3] H. Brooks, article in *Impurities and Imperfections* (American Society for Metals, Cleveland, 1955), p. 1.

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[7] Obtained from the Sigmund Cohn Corporation, Mount Vernon, New York.

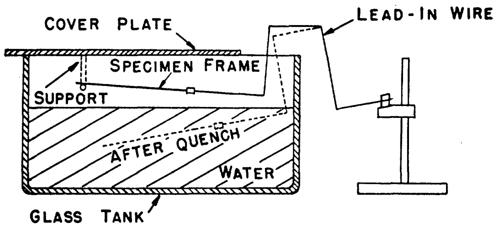

FIG. 2. Sketch of quench tank and specimen prior to and after quenching.

tank itself and a Lucite cover plate. The distance between the specimen frame and the water was 2 cm. To quench the specimen, the stirrup was displaced and the specimen then fell into the water. Its motion was aided by the spring-like nature of the current leads. This arrangement met two critical requirements for efficient quenching: all points of the specimen entered the water simultaneously; and the specimen was kept moving through the water as long as the specimen was above room temperature. The specimen heating current did not interfere with the quench but was turned off manually shortly after the specimen had entered the water.

Measurements of the quenching rates were made by the scheme which Kauffman and Koehler[6] used, i.e., the specimen potential leads were connected to the vertical deflection input of an oscilloscope. A graphical plot of essentially the specimen temperature *vs* time was then obtained. In this way it was found that the cooling rate during the quench was constant and equal to 3×10^4 degrees per second for water.

Longitudinal deformation of the specimen was always less than 5×10^{-4} and did not correlate with the amount of resistivity quenched in. Radial thermal stresses were computed and found to be less than the yield stress for gold.

Changes in the residual resistance of the specimen were measured by the bridge technique developed by Kauffman and Koehler.[6] Figure 3 shows the essential parts of the bridge circuit. After placing the specimen frame into a Dewar of stirred liquid nitrogen, the resistance of the specimen was compared to that of the dummy in the bridge. Variations in the thermal part of the specimen resistance arising from bath-temperature fluctuations were canceled out by like variations in the dummy. The potentials V_{12} and V_{34} were measured with a Rubicon microvolt potentiometer which could detect 10^{-8} volt. The currents I_1 and I_2 were about 0.5 amp each. Current equality was monitored to within 1 part in 50 000 by a galvanometer (across the 1-ohm resistances), and the 0.01-ohm variable resistor served to maintain this balance. The smallest detectible change in resistivity was 10^{-11} ohm cm, which was about 0.02% of the maximum resistivity increase quenched in.

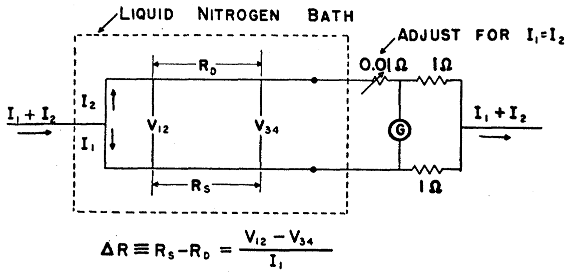

FIG. 3. Schematic diagram of bridge circuit used in resistance measurements.

Annealing was done by transferring the specimen frame to a water bath, which could be set to any temperature between 25°C and 100°C and controlled to ±0.01°C. After a measured interval of time the specimen was removed from the water bath and transferred back to the nitrogen Dewar for measurement. When lower temperatures were needed, a dry ice-acetone mixture was used.

For the measurement of specimen length changes during annealing a special technique was devised, the principle of which is shown in Fig. 4. The specimen, which had an arc-shaped gauge length of 10 cm, was clamped at its ends to a "suspension bar." A simple calculation shows that if such a wire is fixed at its ends, the ratio of an increment in its sagitta h to an increment in its arc length s is approximately given by

$$dh/ds = s/5h. \tag{1}$$

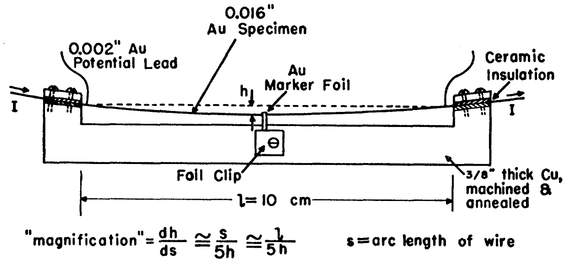

FIG. 4. Details of specimen wire (special frame not shown) mounted in suspension bar for dilatometric measurements.

This means that a change in arc length produces a change in sagitta which is $s/5h$ times as large. For a typical case, $s=10$ cm, $h=0.1$–0.2 cm so that a multiplication of about 10 to 20 times the change of length results. For convenience, h is not measured but only changes in h, referred to the gold foil marker shown in the sketch. These changes were measured with a mean error of 0.3 micron by means of a Gaertner modified creep-testing microscope. The smallest change of length, then, which was detectible with the apparatus was about 0.03 micron, corresponding to a fractional change of length of 3×10^{-7}. Observations on the specimen were made through the window of a constant-temperature bath in which the specimen and suspension bar were immersed. The temperature of the bath was kept at 30.000±0.005°C. To check the linearity of sagitta change with arc-length change and also get dh/ds experimentally it was necessary only to vary the bath temperature. Because of the difference in thermal expansion of the copper suspension bar and the gold wire, an apparent change in specimen length of approximately 0.25 micron per °C results. A typical calibration curve is shown in Fig. 5. Since the bath temperature during an anneal was kept very nearly constant, no dummy was needed for the resistance measurements in this arrangement. One-mil insulated platinum supports spaced every 2.5 cm along the gauge length kept these long wires from sagging when hot, thus decreasing accidental deformation.

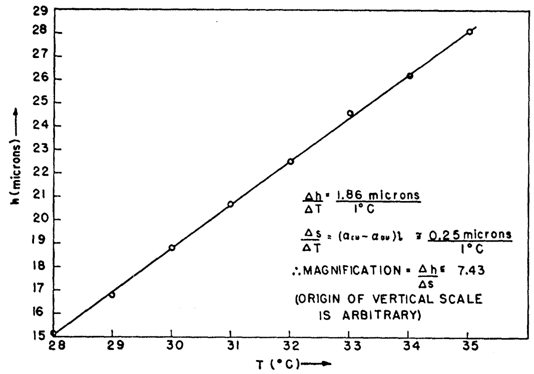

FIG. 5. Sample plot of sagitta *vs* bath temperature for a specimen mounted in suspension bar. Linearity is verified and "magnification" factor determined.

III. RESULTS

A. Quenching

For the range of quench temperatures studied, 450°C to 1000°C, it was found that the resistivity increase on quenching could be described by the equation

$$\Delta\rho = Ae^{-E_F/KT_Q}, \tag{2}$$

where $\Delta\rho$ is the resistivity increase, A is a constant, E_F is the energy required to form the defect, K is Boltzmann's constant, and T_Q is the quench temperature. The justification for calling E_F the energy of formation of the defect comes from statistical mechanics. It gives an expression similar to Eq. (2) for the equilibrium concentration of defects having formation energy E_F, in a solid at temperature T_Q. If it is assumed that the defects are retained during the quench, Eq. (2) follows immediately. To check the goodness of fit of the data to Eq. (2), one may plot the data as $\ln\Delta\rho$ *vs* $1/T_Q$. The points should then fall on a straight line, as is the case in Fig. 6. Values for E_F and A are obtained from the slope and intercept of the line, respectively. Table I summarizes the results for six different specimens. The average results were as follows: $E_F = 0.98 \pm 0.03$ ev, and $A = (4.9 \pm 1.0) \times 10^{-4}$ ohm cm. Errors given are random only.

Attempts were made to find some special systematic errors which might be important. For example, to rule out the possibility that hydrogen (from dissociated H_2O) might have dissolved in the specimen during the quench and thus produced spurious effects, some quenches were made with mercury as the quenching medium. Some surface amalgamation resulted which was quickly removed with nitric acid. The increase in resistance and annealing behavior after the mercury quench were the same (within 10%) as after a water quench. It was concluded that the results were independent of the chemical nature of the quench medium used.

TABLE I. Summary of experimentally determined constants for the equation $\Delta\rho = Ae^{-E_F/KT_Q}$.

Specimen No.	Diameter (in.)	E_F (ev)	A (ohm cm)
1	0.016	0.96	3.2×10^{-4}
2	0.016	0.98	5.4×10^{-4}
3	0.030	1.05	9.5×10^{-4}
4	0.030	0.96	4.1×10^{-4}
6	0.016	0.99	4.8×10^{-4}
7	0.016	0.96	4.1×10^{-4}

Another possible source of resistance increases on quenching could be the impurities initially in the wire. It is conceivable that the resistance increases found on quenching might be due to impurities which precipitate in a slowly cooled wire, but would remain dispersed in

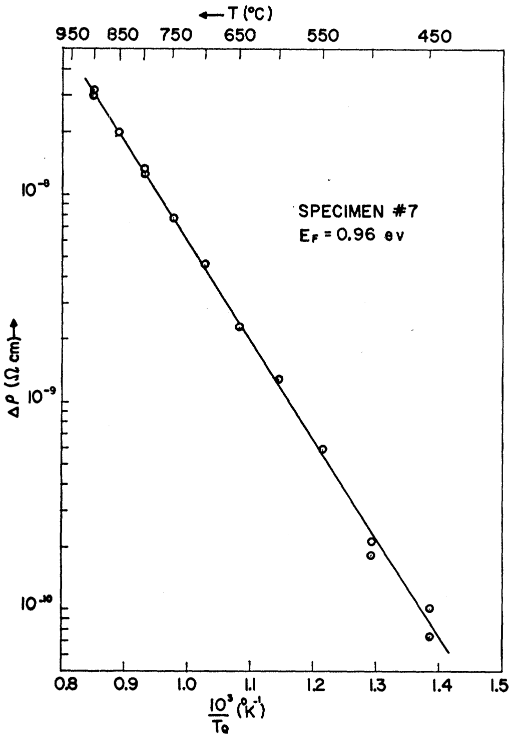

FIG. 6. Semilogarithmic plot of quenched-in resistivity *vs* reciprocal of the absolute quench temperature.

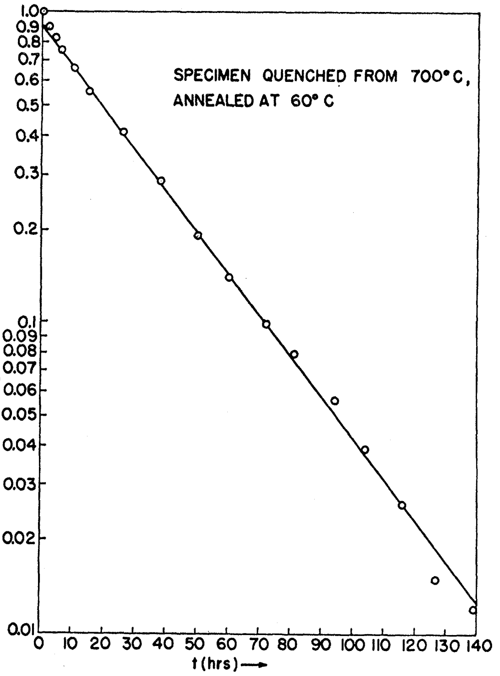

FIG. 7. Semilogarithmic plot of quenched-in resistivity (relative to initial value) *vs* time. Quench temperature was 700°C and annealing temperature was 60°C.

a quenched specimen. To test this idea, a specimen which was quite impure [$\rho(4°\text{K})/\rho(298°\text{K})=0.03$] was quenched. The resistance quenched in was always equal to or *less* than that for a high-purity specimen, demonstrating that the particular impurities present in this impure specimen were not responsible for the quenched in resistance.

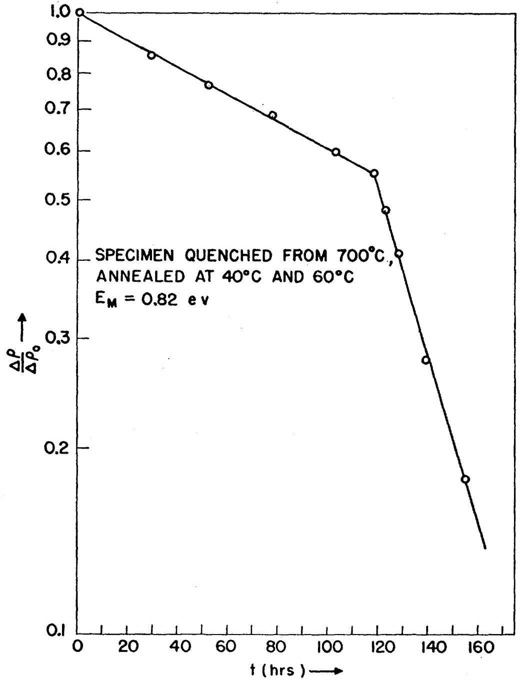

FIG. 8. Influence of annealing temperature on rate of anneal. Specimen quenched from 700°C; annealed first at 40°C, then at 60°C.

Finally, we wished to know whether a change in the quenching rate had an influence on the amount of resistance quenched in. A quench into salt water (10% solution) gave a quenching rate of about 6×10^4 deg/sec, twice that for pure water. When such a quench was used, approximately 15 to 20% more resistance was quenched in. More surprising, though, was the fact that the increase was the same, percentage-wise, for all temperatures checked, i.e., 600°C to 900°C. If vacancies were being lost during the quench, one would expect to lose a much larger fraction of them at 900°C than at 600°C. The essential thing to note here is that since $\Delta\rho$ was larger by a constant factor, the energy of formation, E_F, was not affected. The constant A was, however, increased by 15 to 20%.

B. Annealing

The room-temperature annealing of the quenched-in resistance was found to depend markedly on the temperature from which the specimen was quenched; hence, we shall classify the results according to the quench temperature T_Q.

1. Quenches from below 750°C

(a) The quenched-in resistance decayed exponentially with the annealing time. (See Fig. 7.) Occasionally the initial annealing was slightly faster than exponential for a short time.

(b) The time τ required for one-half of the quenched-in resistance to anneal out was very long, i.e., of the order of hundreds of hours at 40°C.

(c) The lower the quench temperature T_Q, the longer τ was. For example, at 60°C, $\tau=19$ hr for a quench from 700°C and $\tau=50$ hr for a quench from 600°C.

(d) More than 99% of the quenched-in resistance annealed out in the neighborhood of room temperature.

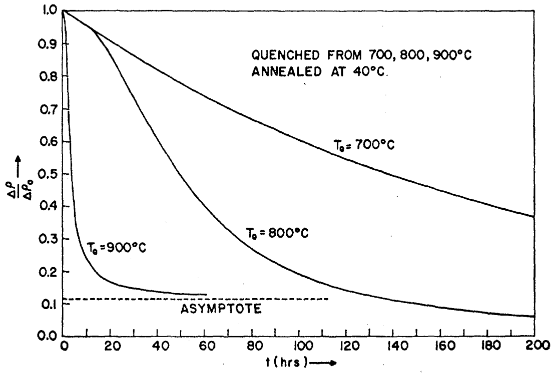

FIG. 9. Quenched-in resistivity (relative to initial value) *vs* time. Quench temperatures 700, 800, and 900°C, annealed at 40°C.

(e) The activation energy for motion of the defect, E_M, was 0.82±0.05 ev. (See Fig. 8.) All energies of motion in this experiment were derived from the data on the assumption that the thermal activation probability entered the rate equation for annealing as follows:

$$dc/dt = -e^{-E_M/KT} f(c), \tag{3}$$

where c is the defect concentration. For $T_Q = 700°\text{C}$, the exponential decay of c with time implies that $f(c)$ is proportional to c, i.e., first-order annealing kinetics. The value of E_M may be obtained by comparing slopes of the $\log\Delta\rho$ *vs* t curves at two different annealing temperatures as in Fig. 8.

(f) The specimen length was observed to decrease slightly during the annealing of quenched-in resistance. This decrease was exponential with time. The proportionality factor between the resistance decrease and the fractional length decrease was approximately 1.3×10^{-3} ohm cm (one determination).

2. *Quenches from 800°C*

A transition in annealing behavior began to show itself at this quench temperature. (See Fig. 9.)

(a) The decay of the quenched-in resistance was quite slow for some time; then a sudden break to a much faster annealing curve (not exponential) occurred. The initial annealing rate was consistent with the rates observed for quenches from 700°C.

(b) The time required for one-half of the quenched-in resistance to anneal out at 40°C was about 49 hours.

(c) About 95% of the quenched-in resistance annealed out in the neighborhood of room temperature.

(d) The activation energy for motion, E_M, was 0.66±0.03 ev. (See Fig. 10.) In this determination it was assumed that the annealing obeyed Eq. (3).

(e) Small amounts of deformation ($\epsilon < 10^{-3}$) speeded up the initial rate of anneal so that the decay curve no longer showed the break described in (a). The annealing rate past the initial region was not appreciably affected, however.

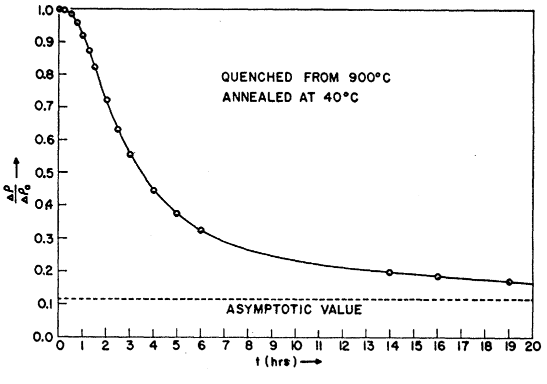

FIG. 11. Quenched-in resistivity (relative to initial value) *vs* time. Quench temperature 900°C, annealed at 40°C.

3. *Quenches from above 850°C*

(a) The decay curve showed no sudden breaks but the decay *rate* increased continuously from some very small value to a maximum and then decreased slowly to zero. (See Fig. 11.)

(b) The time required for one-half of the quenched-in resistance to decay was quite short, i.e., of the order of a few hours at 40°C.

(c) The higher the quench temperature, the shorter τ was. For example, at 40°C, $\tau = 3.5$ hr for a quench from 900°C, and $\tau = 0.5$ hr for a quench from 1000°C.

(d) About 90% of the quenched-in resistance annealed out in the neighborhood of room temperature. The remaining 10% annealed somewhere between 500°C and 800°C.

(e) The activation energy for motion of the defect, E_M, was 0.63±0.06 ev for a quench from 925°C and 0.60±0.04 ev for a quench from 1000°C. (See Fig. 12.) As before, Eq. (3) was assumed valid for the annealing process.

(f) The specimen length decreased in exactly the same manner as the specimen resistance at all stages of

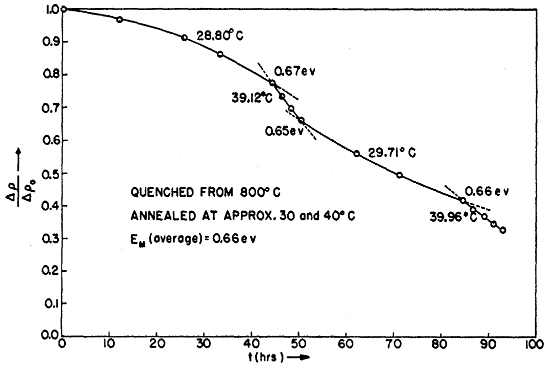

FIG. 10. Energy of motion determination for a specimen quenched from 800°C, annealed at approximately 30 and 40°C.

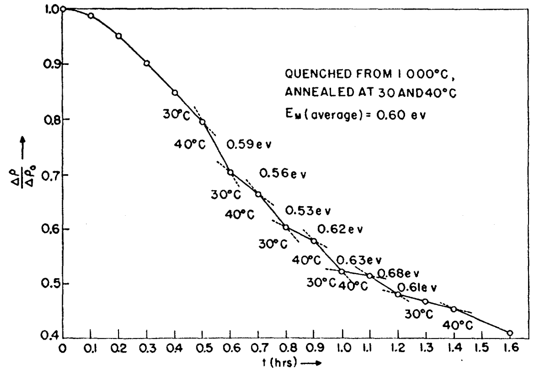

FIG. 12. Energy of motion determination for a specimen quenched from 1000°C, annealed at 30 and 40°C.

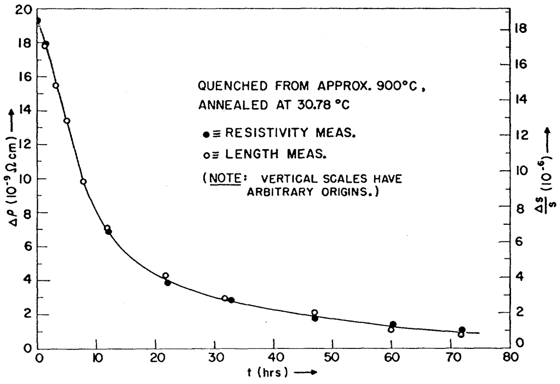

FIG. 13. Quenched-in resistivity and fractional length decrease *vs* time. Quench temperature 900°C, annealed at approximately 30°C.

the annealing process. (See Figs. 13 and 14.) The curves were superimposable with a proportionality factor between the resistivity change and the fractional-length change of 1.00×10^{-3} ohm cm. (Average of three determinations.)

(g) Small amounts of deformation speeded up the *initial* annealing rate as described in part 2, (a). The long specimens used for the length-change studies tended to show this effect, as in Fig. 13. When special precautions were taken to avoid deformation (see Experimental Procedure), the slower initial annealing rate once more became evident, as in Fig. 14.

(h) For an impure specimen $\rho(4°\mathrm{K})/\rho(298°\mathrm{K})=0.03$ the decay of resistance was very rapid ($\tau=1$ hr at 25°C), and was approximately exponential, with a residue of about 25% of the original resistivity increase remaining after an anneal at room temperature. The energy of motion was 0.67 ± 0.06 ev.

(i) An isochronal anneal revealed only *one* prominent annealing process near room temperature. In this anneal, a specimen was quenched from 900°C and annealed for one hour at each of a series of increasing temperatures, starting at $-200°$C and ending at $+100°$C. After each anneal the resistivity was measured with the results as shown in Fig. 15.

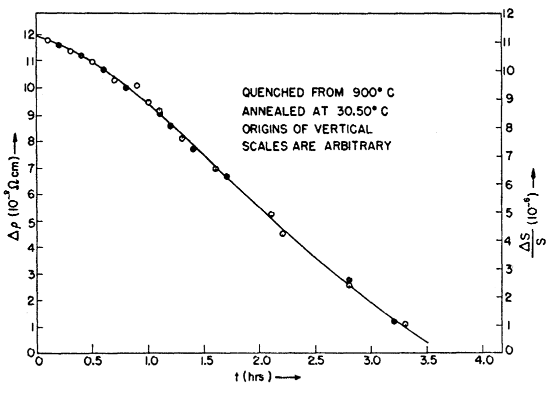

FIG. 14. Same as Fig. 13 except special support loops used on specimen to avoid deformation.

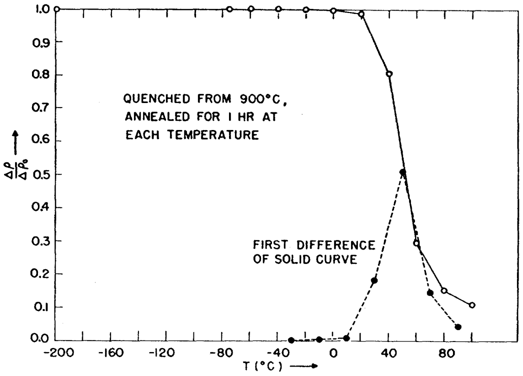

FIG. 15. Isochronal anneal of quench from 900°C showing major annealing process near room temperature.

IV. SUMMARY

A. Thermally activated defects may be trapped in gold by quenching rapidly from high temperatures. Their energy of formation is about 1.0 ev.

B. Motion of these defects to sinks is thermally activated and occurs at an easily measured rate in the neighborhood of 40°C. Their energy of motion varies from 0.8 ev for a quench from 700°C to 0.6 ev for a quench from 1000°C.

C. The annealing "half-life" at 40°C varies from 140 hr for a quench from 700°C to about $\frac{1}{2}$ hr for a quench from 1000°C.

D. The annealing kinetics are first order for a quench from 700°C or below but are more complicated for quenches from higher temperatures.

E. The volume of the specimen diminishes during annealing in exactly the same manner as the resistivity whether the kinetics are simple or not. The proportionality constant between resistivity and fractional volume change is about 3×10^{-4} ohm cm.

An interpretation of these data in terms of single and multiple vacancies appears in the following paper.[8]

ACKNOWLEDGMENTS

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[8] Koehler, Seitz, and Bauerle, following paper [Phys. Rev. **107**, 1499 (1957)].