

Measurement of Equilibrium Concentrations of Lattice Vacancies in Gold

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The linear thermal expansion of a 99.999% gold bar has been measured throughout the range 15° to 1057°C by direct observation of the length expansion $\Delta L/L$, with filar micrometer microscopes and by measurement of the lattice parameter expansion $\Delta a/a$, by x-ray diffraction with a rotating-single-crystal method. The expansions agree within the experimental precision of about 1:10⁵ at the lower temperatures. However, the values of thermal expansion obtained are about 1.5% larger than those in the literature. At the higher temperatures ($\Delta L/L - \Delta a/a$) becomes positive, proving that thermally-generated defects are formed which are predominantly vacant lattice sites. The net added concentration of substitutional atomic sites, $\Delta N/N = 3(\Delta L/L - \Delta a/a)$, just below the melting temperature, is $(7.2 \pm 0.6) \times 10^{-4}$ as obtained by an extrapolation of the data of only 6°C. $\Delta N/N$ can be described by $\exp(1.0) \exp(-0.94 \text{ ev}/kT)$. These results are inde-

pendent of any aggregation of the defects and of any lattice dilatation about the individual defects. Just below the melting temperature, more than 80% of the vacant sites are single vacancies if the divacancy and trivacancy binding energies are less than 0.4 ev and 1.0 ev, respectively.

The present concentrations are about 40% larger than those reported by DeSorbo from a calorimetric study of quenched foil. A critical assessment of the relationship between the present equilibrium measurements and results obtained by quenching methods is attempted. Combination of present $\Delta N/N$ values with $\Delta \rho$ and $(\Delta L/L)/\Delta \rho$ values of Bauerle and Koehler and with $\Delta L/L$ values of Takamura on quenched and annealed wires gives an electrical resistivity $\rho_v = 1.5 \pm 0.3 \text{ } \mu\text{ohm cm/at.}\%$ of vacancies and a volume expansion $\chi = 0.45 \pm 0.10$ atomic volume/vacancy.

I. INTRODUCTION

GOLD has been the subject of many quenching investigations aimed at retaining under well-defined conditions the predominant lattice defect present in high-temperature thermal equilibrium in a close-packed metal. In addition, studies of interactions of the retained defects with themselves, dislocations, stacking faults, and so on, have been made. Gold has proven to be a most suitable metal for quenching studies of this type because of the relatively large effects obtainable, because of its resistance to oxidation, and because many of these changes introduced by quenching anneal in a convenient temperature range above room temperature.^{1,2}

A great variety of properties of quenched gold have now been investigated. Among very recent examples of experimental work are calorimetric studies of the annealing of quenched foils,^{3,4} dilatometric measurements on quenched foils⁵ and wires⁶ during annealing, measurements of electrical resistance changes in quenched wires annealed under hydrostatic pressure,⁷ measurements of electrical resistance changes during the annealing of quenched wires which were subsequently deformed,⁸ the examination of thin quenched foils by

transmission electron microscopy,^{9,10} study of internal friction in quenched wires,¹¹ measurements of the time dependence of the appearance of residual electrical resistivity increments in pulse-heated wires,¹² and studies of the annealing of quench-hardening in quenched wires.¹³ In addition, related work, such as irradiation damage studies of residual electrical resistivity changes and some impurity and self-diffusion measurements, has given further information about defects in gold. Many of these experiments have been reported along with accompanying proposed interpretations, and, in addition, a number of theoretical studies of quenching of an interpretive nature have appeared.¹⁴⁻¹⁶

The observed phenomena have proven to be very complex in detail, and it is clear that well-defined constraints upon possible interpretations would be useful. In several cases circular arguments have appeared in the interpretation of results because of a lack of knowledge concerning the fundamental physical properties of the predominant defects themselves.

Among the primary facts which have been lacking for gold are (1) an unequivocal identification of the predominant thermally-generated defects, (2) a determination of their concentrations under thermal equilibrium conditions, and (3) an estimation of their formation energy and formation entropy from measurements under thermal equilibrium conditions. The present work constitutes a direct determination of these facts in a

¹ See the review papers in *Vacancies and Other Point Defects in Metals and Alloys* (The Institute of Metals, London, 1958).

² The most complete early quenching study was that of J. E. Bauerle and J. S. Koehler, *Phys. Rev.* **107**, 1493 (1957).

³ W. DeSorbo, *Phys. Rev.* **117**, 444 (1960).

⁴ V. A. Pervakov and V. I. Khotkevich, *Doklady Akad. Nauk S.S.S.R.* **134**, 1328 (1960) [translation: *Soviet Phys.-Doklady* **5**, 1051 (1961)].

⁵ B. B. Lazarev, O. N. Ovcharenko, and I. R. Kredchuk, *Fiz. Metal. i Metalloved. Akad. Nauk S.S.S.R., Ural. Filial* **7**, 154 (1959) [translation: *Phys. of Metals and Metallography* **7**, 149 (1960)].

⁶ J. Takamura, *Acta Met.* **9**, 547 (1961).

⁷ R. M. Emrick, *Phys. Rev.* **122**, 1720 (1961).

⁸ S. Yoshida and J. S. Koehler, *Acta Met.* **8**, 878 (1960); M. Meshii and J. W. Kauffman, *ibid.* **8**, 815 (1960).

⁹ J. Silcox and P. B. Hirsch, *Phil. Mag.* **4**, 72 (1959).

¹⁰ R. M. J. Cotterill, *Phil. Mag.* (to be published).

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

¹² J. J. Jackson and J. S. Koehler (to be published).

¹³ T. Mori, M. Meshii, and J. W. Kauffman, *Acta Met.* **9**, 71 (1961).

¹⁴ J. S. Koehler, F. Seitz, and J. E. Bauerle, *Phys. Rev.* **107**, 1499 (1957); V. I. Vladimirov, *Fiz. tverdogo Tela* **2**, 157 (1960) [translation: *Soviet Phys.—Solid State* **2**, 145 (1960)]; G. J. Dienes and A. C. Damask (to be published).

¹⁵ H. Kimura, R. Maddin, and D. Kuhlmann-Wilsdorf, *Acta Met.* **7**, 145 (1959).

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

manner which requires no *ad hoc* assumptions. Uncertainties introduced by the process of quenching are eliminated.

Values of relative linear thermal expansion $\Delta L/L$ and relative x-ray lattice thermal expansion $\Delta a/a$ have been measured on a high-purity gold bar. If substitutional atomic sites are created or destroyed due to the thermal generation of point defects, then the net added concentration of such sites is given by the difference

$$\Delta N/N = 3(\Delta L/L - \Delta a/a). \quad (1)$$

This result is independent of the lattice relaxation about the defects,¹⁷ even for the possible case of large relaxations and of changes in the elastic properties of the lattice.¹⁸ The sign of $\Delta N/N$ tells whether lattice vacancy or interstitial atom type defects predominate. If the temperature dependence of $\Delta N/N$ can be determined, then an estimate may be made of the formation energy E_j^f , and the formation entropy S_j^f , exclusive of configurational entropy, of the predominant defect, because the concentration of defects of type j is given by

$$c_j = g_j \exp(-G_j^f/kT) = g_j \exp(S_j^f/k) \exp(-E_j^f/kT), \quad (2)$$

where k is Boltzmann's constant and T is the absolute temperature. The factor g_j is determined by the symmetry of the defect. Measurements of this type have been reported by the writers on the metals aluminum^{17,19} and silver.²⁰ Because the concentrations are of order 10^{-4} , the relative linear expansions must be measured with a precision of 10^{-5} , for which considerable care is required.

II. EXPERIMENTAL METHOD

Simultaneous measurements of $\Delta L/L$ and $\Delta a/a$ on a long bar-shaped specimen at temperatures in the range 15° to 1057°C were made using techniques similar to those already applied to aluminum¹⁷ and to silver.²⁰ Further discussion of the method and schematic diagrams of the apparatus appear in these earlier papers.

A. Furnace

A resistance-heated horizontal tube furnace having a cylindrical spectrographically pure graphite core was used. The core had a very smoothly machined chamber which provided essentially unconstrained support of the long bar-shaped specimen. A gas-tight Inconel jacket minimized gas convection currents about the sample and contained the nearly static prepurified nitrogen atmosphere used for protection of the graphite against oxidation. The jacket had quartz windows for the length

measurements and a polyester film window for passage of the x-ray beam.

Temperatures were measured by a butt-welded Pt *versus* Pt 10% Rh thermocouple (Sigmund Cohn and Company "reference grade," having specified accuracy 0.1%) mounted in a quartz tube placed parallel to the specimen length and located in the graphite furnace core about 1 mm from the upper specimen surface. This same thermocouple was used in previous work on aluminum¹⁷ and silver.²⁰ Differences in temperature along the specimen length could be readily measured by sliding the thermocouple junction along inside the tube parallel to the furnace axis.

Temperature variations along the specimen length and during the time required for an expansion measurement were maintained at less than $\pm 0.2^\circ\text{C}$. Further, these variations were measured and suitable corrections could then be applied. The linear thermal expansion coefficient of gold is less than $2 \times 10^{-5} (\text{C}^\circ)^{-1}$; such corrections to $\Delta L/L$ or to $\Delta a/a$ due to space or time variations of temperature were therefore never larger than 4×10^{-6} and were accurate to 1×10^{-6} . The advantage of the present method is that measurements of $\Delta L/L$ and $\Delta a/a$ are referred to a common identical temperature scale. Temperature measuring errors are, therefore, believed to be negligible in the measurement of the difference $(\Delta L/L - \Delta a/a)$. The entire apparatus was stabilized by regulation of the room temperature within $\pm 1^\circ\text{C}$.

B. Specimen

The gold specimen was prepared from material of nominal purity 99.999%, supplied by Sigmund Cohn and Company. The supplier lists this gold as "chemically pure, 99.999% gold," and it is presumably similar to the material from the same source used by Bauerle and Koehler² and by DeSorbo.³ Spectrographic analysis of the as-received gold by R. H. Bell of Lucius Pitkin, Inc., gave the following results: present in the range 1 to 9 parts per million, Cu and Ag; checked but not detected, Mg, Al, Si, Ti,[†]V, Cr, Mn, Fe, Co, Ni, Zn, Ga, Ge, As, Zr, Mo, Pd,[‡]Cd, In, Sn, Sb, W, Pt, Pb, Bi, and Th. Reanalysis by identical methods of the specimen after preparation gave the same results.

The apparatus used requires a specimen, 50 cm long by 1.27 cm by 1.27 cm, which has a sound, nonporous structure and a large grain of particular crystal orientation near the center of the bar at the x-ray port. Such a specimen was prepared by the melting and controlled solidification procedure which had been successfully applied to silver.²⁰ The method retains the advantages of directional solidification while avoiding any large hydrostatic pressure either on the hot solid or on the solid-liquid interface.

The gold was melted and cast in a prepurified nitrogen atmosphere by rapid cooling from one end in a horizontal spectrographically pure graphite mold. The temperature gradient along the bar (about 10 deg/cm) and

¹⁷ R. O. Simmons and R. W. Balluffi, Phys. Rev. **117**, 52 (1960).

¹⁸ R. W. Balluffi and R. O. Simmons, J. Appl. Phys. **31**, 2284 (1960).

¹⁹ R. O. Simmons and R. W. Balluffi, J. Appl. Phys. **30**, 1249 (1959).

²⁰ R. O. Simmons and R. W. Balluffi, Phys. Rev. **119**, 600 (1960).

the cooling rate (about 50 deg/min) were chosen to produce an average grain size of about 1.5 cm. The grains were nucleated along both sides of the sample so that no single grain boundary occupied the entire transverse cross section of the bar. This provided an interlocking structure of the large grains composing the specimen which was useful in maintaining stability against irreversible length changes due to possible grain boundary sliding at the highest temperatures. The same method can produce single-crystal specimens under less drastic cooling conditions, but the probability of obtaining a crystal of the required orientation for the x-ray measurement is greatly reduced.

The large grain used for the x-ray measurements had a [211] direction inclined only 1° from the specimen surface normal. The ends of the as-cast specimen were chemically polished to provide a smooth surface for the reference marks used in the length measurements. Polishing was done by immersion in a warm concentrated solution of gold chloride in aqua regia. Great care was taken subsequent to casting of the long soft bar to ensure that it was not appreciably deformed by the ensuing operations of etching, x-ray orientation, polishing, reference marking, direct gauge-length measurement, and insertion in the furnace.

C. Length Expansion Measurement

Changes in length $\Delta L/L$ were measured directly by observing changes in the spacing of reference marks located near the ends of the specimen. A rigidly mounted parallel pair of 60 \times filar micrometer microscopes was used to look at symmetrical 40- μ wide pyramidal indentations in the specimen surface. The microscope spacing was kept constant by a massive Invar mounting. An occasional check of constancy during the experiment was made by examination of an Invar standard.

The initial specimen gauge length was measured to an accuracy of 1.4×10^{-4} with a high-precision cathetometer made by Wild Heerbrugg. The specimen shape was made to conform to the flat graphite support by annealing for six hours above 1020°C. An irreversible increase in length of less than 3×10^{-5} occurred during this treatment; the specimen was, therefore, essentially completely relaxed during all of the preparatory operations.

The most important factor limiting the accuracy of measurement of $\Delta L/L$ by the present technique is the required dimensional stability of the specimen. This dimensional stability includes that of the specimen reference marks which may be subject to possible changes in appearance or configuration due to high-temperature processes. Because of the smooth and unconstrained support of the specimen by the graphite, the rather large and symmetrical character of the reference marks, and the absence of any required temperature corrections applied to the measuring apparatus itself, the error in $\Delta L/L$ is kept near 1×10^{-5} , even for

repeated thermal cycling between room temperature and the melting temperature.

In the present work, because of rather limited access to the specimen reference marks through the viewing holes in the graphite core, the marks were illuminated in a manner different from previous work on aluminum¹⁷ and silver.²⁰ At lower temperatures essentially vertical illumination from tungsten filament lamps was used, while at high temperatures the marks were self-illuminated by thermal radiation. Through the lower and the higher temperature intervals the visibility of the marks was excellent. Further, the appearance of the significant features of the marks was identical in the higher and in the lower temperature intervals. In an intermediate temperature interval from about 750°C to 900°C, however, the visibility was somewhat impaired; the accuracy of the macroscopic expansion measurements in this interval therefore was reduced to about 3×10^{-5} .

D. Lattice Expansion Measurement

The rotating single-crystal technique employing film was used with the same geometry as in previous work on silver.²⁰ The (422) crystal planes gave Bragg angles θ , in the interval between about $84\frac{2}{3}^\circ$ and 78° for Ni $K\alpha_1$ radiation ($\lambda = 1.65784 \text{ \AA}$). Film exposure times varied between only 2 minutes (at a specimen temperature of 15°C) and 12 minutes (at 1057°C) for 30 kv, 13 ma power applied to a standard General Electric Company CA-7 tube.

The present method is not used to measure absolute lattice parameters (although it can do so with an accuracy of about 1×10^{-4}). Rather, changes in lattice parameter $\Delta a/a$ are very sensitively indicated, the accuracy being near 1×10^{-5} . Relative changes $\Delta a/a$ are matched to the observed length expansions $\Delta L/L$, in a large temperature interval, in the present case 15°C to 600°C, where appreciable concentrations of thermally-generated defects are not present. The matching is made by the choice of a single reference lattice parameter, $a(T_r)$, chosen at some reference temperature, T_r . The choice in the present case was $a(20^\circ\text{C}) = 4.07824 \text{ \AA}$. This choice corresponds exactly, after temperature correction, to the "best" value for gold of $a(25^\circ\text{C}) = 4.07855 \text{ \AA}$ of Pearson's compilation.²¹

III. EXPERIMENTAL RESULTS

Measurements of $\Delta L/L$ and $\Delta a/a$ for gold were made in the temperature interval 15°–1057°C, the highest temperature of measurement being within 6 degrees of the melting point. Eighty-seven $\Delta a/a$ measurements were made during two heating runs and two cooling runs while seventy-four $\Delta L/L$ measurements were made during the second heating run and the two cooling runs. The relative expansions were plotted versus temperature, and best smooth curves were drawn through the

²¹ W. B. Pearson, *Lattice Spacing and Structure of Metals and Alloys* (Pergamon Press, New York, 1958).

data points. The mean absolute deviations of the experimental points from the smooth curves were 11×10^{-6} for the $\Delta L/L$ data and 10×10^{-6} for the $\Delta a/a$ data. The respective maximum deviations were 39×10^{-6} and 33×10^{-6} . As explained in the previous section, the curves coincided within experimental error in the temperature interval 15° – 600°C in which a total of ninety-two $\Delta L/L$ and $\Delta a/a$ data points showed a mean absolute deviation of 11×10^{-6} from a common curve.

No evidence was obtained of any systematic lack of reversibility during heating or cooling, once the specimen shape was stabilized during the first heating as described in Sec. II. C.

The specimen heating and cooling rates employed between measurements were sometimes as large as one degree per minute, and measurements were sometimes taken immediately after arrival at the new temperature. Possible "isothermal expansion" effects, which have been reported in high-purity gold following comparable heating²² might therefore affect the results. A separate study which closely duplicated the conditions of the expansion work²² was therefore carried out. Although less than 10% of the reported "isothermal expansion" could have been detected, no such effect was found.²³

Our thermal expansion values are compared to those

TABLE II. Macroscopic linear thermal expansion of gold.

T (°C)	Present work	[$\Delta L/L$ (20°C)] $\times 10^3$			
		(a)	(b)	(c)	(d)
50	0.43	0.43	...
100	1.16	1.16	1.15	1.15	1.13
150	1.89	1.88	...
199	2.63	2.57
200	2.65	2.64	2.61	2.62	...
250	3.42	3.37	...
300	4.19	4.16	4.12	4.14	...
301	4.21	4.13
350	4.98	4.91	...
399	5.77	5.68
400	5.78	5.73	5.69	5.70	...
450	6.60	6.51	...
500	7.45	7.34	7.32	7.33	...
506	7.55	7.41
550	8.29	8.16	...
599	9.13	9.02
600	9.15	...	9.02	9.02	...
650	10.04	9.89	...
700	10.95	...	10.79	10.78	...
701	10.97	10.75
730	11.51	11.27
750	11.89	11.68	...
800	12.85	...	12.65	12.61	...
850	13.84	13.56	...
900	14.85	...	14.60	14.53	...
950	15.91	15.53	...
1000	17.01
1050	18.15
(1060)	(18.38)

^a See reference 26.

^b See reference 27.

^c See reference 28.

^d See reference 29.

TABLE I. Lattice parameter thermal expansion of gold.

T (°C)	Present work	[$\Delta a/a$ (20°C)] $\times 10^3$	
		(a)	(b)
50	0.43
75	0.79	...	0.65
100	1.16	1.2	...
122	1.48	...	1.31
150	1.89
174	2.25	...	2.13
200	2.65	2.9	...
245	3.34	...	3.18
250	3.42
300	4.19	4.3	...
309	4.33	...	4.12
350	4.98
363	5.19	...	4.95
400	5.78	6.0	...
401	5.80	...	5.45
450	6.60
500	7.45	7.6	...
550	8.29
600	9.15	9.2	...
650	10.04
700	10.94	11.0	...
750	11.87
800	12.81	12.9	...
850	13.77
900	14.77	14.7	...
950	15.80
1000	16.85	16.7	...
1050	17.93	17.7	...
(1060)	(18.15)

^a Values picked off smooth curve in reference 24.

^b See reference 25.

²² H. U. Astrom, Arkiv Fysik 18, 465 (1960).

²³ R. O. Simmons and R. W. Balluffi (to be published).

of other investigators^{24–29} in Tables I and II. All of the relative expansions have been referred to 20°C using a value of 13.9×10^{-6} per degree for the expansion coefficient near room temperature.

The close agreement between $\Delta L/L$ and $\Delta a/a$ values in a lower temperature range is shown in Fig. 1. At high temperatures, $\Delta L/L$ is larger than $\Delta a/a$, as shown in Fig. 2, because of the thermal generation of vacancy-type lattice defects. The reversible nature of the measured divergence between the two types of expansion measurements guarantees that the measured differences correspond to the equilibrium values. Values of $\Delta N/N = 3(\Delta L/L - \Delta a/a)$ for the present thirteen pairs of measurements in the range 900° – 1057°C are shown in Fig. 3. In each pair the measurement made at the lower temperature was corrected to the higher temperature of the other measurement by means of an expansion coefficient obtained from the appropriate smooth curve in Fig. 2. These temperature corrections averaged less than 0.7 degree, or less than 1.5×10^{-5} in relative expansion, and introduced negligible error because the

²⁴ H. Esser, W. Eilender, and K. Bungardt, Arch. Eisenhüttenw. 12, 157 (1938).

²⁵ A. Gott, Ann. Physik 41, 520 (1942).

²⁶ A. Müller, Physik. Z. 17, 29 (1916).

²⁷ J. B. Austin, Physics 3, 240 (1932).

²⁸ H. Esser and H. Eusterbrock, Arch. Eisenhüttenw. 14, 341 (1941).

²⁹ F. C. Nix and D. MacNair, Phys. Rev. 60, 597 (1941).

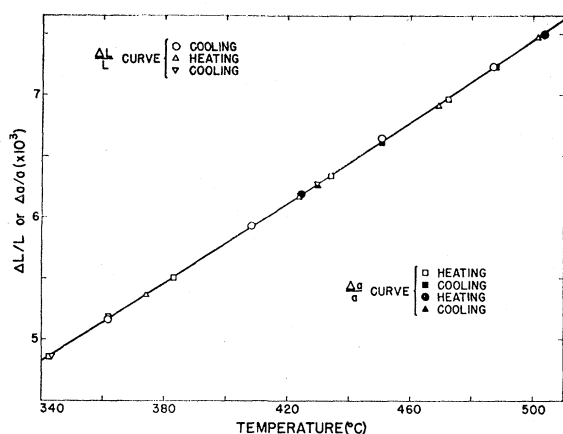


FIG. 1. Measured length expansion $\Delta L/L$ and lattice parameter expansion $\Delta a/a$ versus temperature in the interval 340°–510°C. The x-ray and length expansions agree within experimental error. A number of $\Delta a/a$ data points are not shown because they essentially coincide with corresponding $\Delta L/L$ data points and cannot be clearly shown. The omitted points include; one \blacksquare point at 408.6°C; two \bullet points at 374.4° and 468.9°C; one \blacktriangle point at 342.8°C.

$\Delta L/L$ and $\Delta a/a$ measurements refer to a common temperature scale. The straight line drawn through the points has the equation

$$\Delta N/N = \exp(1.0) \exp(-0.94 \text{ ev}/kT). \quad (3)$$

The estimated accuracy of the $\Delta N/N$ values ranges from about 8% at the highest temperatures to about 25% at the lowest temperature. Therefore the straight line is suggested by and is consistent with the measurements but is not determined by them with high accu-

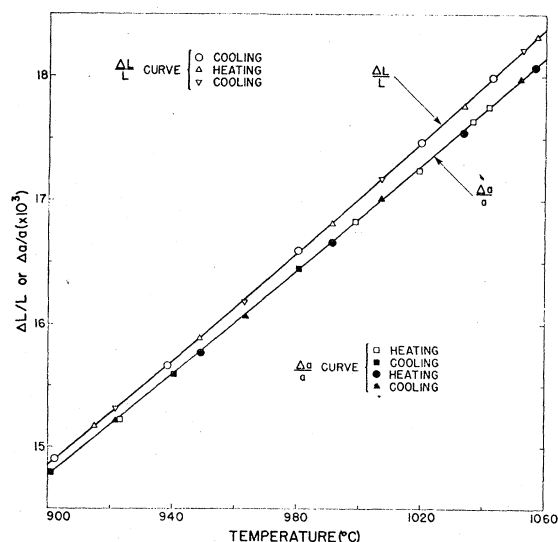


FIG. 2. Measured length expansion $\Delta L/L$ and lattice parameter expansion $\Delta a/a$ versus temperature in the interval 900°–1060°C. $\Delta L/L$ becomes larger than $\Delta a/a$ at the highest temperatures corresponding to the thermal generation of lattice vacancies. The melting temperature of gold is 1063°C.

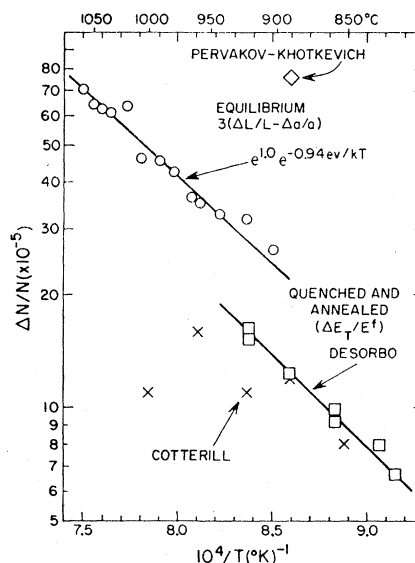


FIG. 3. Atomic fraction of vacant lattice sites $\Delta N/N$ versus inverse temperature in gold. The present equilibrium values of $\Delta N/N = 3(\Delta L/L - \Delta a/a)$ were computed directly from pairs of corresponding expansion measurements. DeSorbo³ measured total energy release in quenched foil ΔE_T during annealing near 55°C and used $E_f = 0.97$ ev. The value designated by \diamond is reported in calorimetric work on quenched wire of Pervakov and Khotkevich.⁴ Cottrell's concentrations¹⁰ were deduced from measured densities of stacking fault tetrahedra in quenched and annealed foils.

racy. The values of $\Delta N/N$ are very significant, however, and extensive discussion and comparison with the results of other types of measurements appears in Sec. V.

IV. DISCUSSION OF THERMAL EXPANSION DATA

Inspection of Tables I and II shows several discrepancies between the present expansion data and previous results. It is therefore useful to consider these results in some detail.

The two previous investigations of lattice parameter expansion, $\Delta a/a$, appear to have been of relatively low precision. The results of Esser *et al.*²⁴ extend to 1050°C, a hundred degrees higher than any other expansion study, but are given only on a small graph. The present $\Delta a/a$ values agree with Esser *et al.*, within the apparent accuracy of their results. The values of Gott²⁵ are quite low. Both of the previous x-ray measurements used the Hull-Debye-Scherrer technique.

The present values of $\Delta L/L$ are higher than any of those previously reported.^{26–29} There is approximate agreement, at least for temperatures below 800°C, between Austin²⁷ and Esser and Eusterbrock,²⁸ while the results of Nix and MacNair²⁹ are slightly smaller. The present measurements show an approximately systematic deviation of about 1.5% above the average of the previous results in the temperature range below 900°C. While the cause of this disagreement has not been determined, some possible explanations can be excluded: (1) A simple temperature error in the present work,

proportional to the temperature difference from the ice point reference temperature, could not account for the 1.5% disagreement because $\Delta L/L$ and $\Delta a/a$ measurements were made on the unmelted bar within less than 0.6% of the apparent melting temperature. (2) An error of 1.5% in the measurement of the gauge length, L , of the sample at 20°C would have led to a systematic error in all $\Delta L/L$ values. However, this length was remeasured by an independent method after the experiment and found to be the same as that determined earlier using the high-precision cathetometer.

Some other remarks are pertinent to the discrepancies noted here. (1) The use of an average of the previous $\Delta L/L$ values to normalize the present $\Delta a/a$ values would require an unreasonable choice of the reference lattice parameter: $a(20^\circ\text{C}) = 4.077\ 60\ \text{\AA}$, which is 1.4×10^{-4} smaller than the accepted value.²¹ In contrast to this the excellent $\Delta a/a$ and $\Delta L/L$ agreement reported in Sec. III was obtained using the accepted "best" value. (2) While for platinum the results of Austin²⁷ below 800°C agree with those of Esser and Eusterbrock²⁸ and of Holborn and Day,³⁰ and while for copper the results of Nix and MacNair²⁹ below 500°C agree with those of Esser and Eusterbrock,²⁸ it is generally recognized that for most substances the results of the latter authors are about 2% low. (3) Temperature measurements by Austin²⁷ and by Nix and MacNair²⁹ were made indirectly by means of a silica refraction thermometer. Further, both these investigators employed Fizeau interferometers which, while yielding reliable expansion coefficients, are quite troublesome to use for the very large integral expansions of concern here. (4) Interferometers and dilatometers may stress the sample locally, producing irreversibility at high temperatures; Austin's results on platinum²⁷ clearly show such effects above 800°C. (5) High-temperature expansion measurements by different methods in different laboratories do not generally agree within better than a few percent³¹ so that the apparent agreement between the limited number of previous measurements on gold could simply be fortuitous. (6) Measurements of $\Delta a/a$ at very high temperatures, if properly performed with accurate knowledge of sample temperature, are probably more accurate than $\Delta L/L$ measurements. Our previous values of $\Delta a/a$ for silver²⁰ show excellent agreement with the standard work of Hume-Rothery and Reynolds³² in which great care was taken with temperature calibration.³³

We emphasize that the quantity of major interest in the present work is the difference between $\Delta L/L$ and

$\Delta a/a$. Systematic errors in the integral expansions $\Delta L/L$ or $\Delta a/a$ of the type discussed above will, of course, have some effect on the difference $(\Delta L/L - \Delta a/a)$. However, the normalization technique used in the present work keeps such possible effects small. For example, if values of $\Delta L/L$ (and consequently also $\Delta a/a$) were used which are 1.5% smaller than the present values in the range 15°–600°C, then $\Delta N/N$ at the melting temperature would be reduced to 5.6×10^{-4} , about 20% smaller than the value reported here.

V. CONCENTRATIONS AND PROPERTIES OF LATTICE DEFECTS

We now consider the information about lattice defects which can be obtained from the present results. First, the measured total defect concentrations are compared to the results of previous work. Next, the relative abundance of monovacancies is considered as a function of the binding energies of the possible vacancy clusters which may also be present in thermal equilibrium. Then values of the monovacancy formation energy and entropy are derived. Next, the results of different quenching investigations are considered, and comparisons are made between the present equilibrium measurements and the quenching results. Finally, some derived values of monovacancy properties are obtained.

A. Total Defect Concentration

From the experimental results it is clear that the predominant thermally-generated defects are of vacancy type; $\Delta N/N$ is positive at high temperatures. A comparison between the present total defect concentration values and the results of the other available experiments yielding absolute concentrations is shown in Fig. 3.

The direct calorimetric study of DeSorbo³ comprised measurements of total energy release ΔE_T , during annealing near 50°C of 0.38-mm thick foil quenched from temperatures in the range 820° to 920°C. DeSorbo's straight line, having a slope corresponding to an apparent defect formation energy of $E_f = 0.97\ \text{ev}$, is also shown in Fig. 3. Defect concentrations were deduced using the relation $\Delta E_T/0.97\ \text{ev}$.

The present defect concentrations are 40% larger than those obtained by DeSorbo. There are several factors which could contribute to this apparent discrepancy. (1) DeSorbo notes that his quenching rate was smaller than that of Bauerle and Koehler. The latter authors quenched 0.41- and 0.76-mm diam wires at two different rates and found that the defect concentration increased with quenching rate. If one assumes that such foils and wires behave similarly, DeSorbo's values of $\Delta N/N$ would be increased by about 20% according to an extrapolation of the rates. (2) DeSorbo estimated the accuracy of his reported values as 10 to 15%. However, from 25 to 40% of the magnitudes of his ΔE_T values consist of estimates of energy release obtained by extrapolation beyond the actual range of

³⁰ L. Holborn and A. L. Day, Ann. Physik 4, 104 (1901).

³¹ W. Hume-Rothery, Proc. Phys. Soc. (London) 57, 209 (1945).

³² W. Hume-Rothery and P. W. Reynolds, Proc. Roy. Soc. (London) A167, 25 (1938).

³³ The fact that the value of 1063°C fixed by international agreement for the gold fusion point is apparently about 1.5 degrees low on the thermodynamic scale {A. N. Gordov, A. S. Arzhanov, and U. V. Diikov, Doklady Akad. Nauk S.S.S.R. 133, 811 (1960) [translation: Soviet Phys.-Doklady 5, 871 (1961)]} is, of course, irrelevant.

TABLE III. Collected experimental values of lattice vacancy properties in fcc metals.

Metal	$(\Delta N/N) \times 10^4$ at melting point	E_{v1}^f (ev) Present method ^a	E_{v1}^f (ev) Quenching ^f	S_v^f/k	$\Delta\rho/c_{v1}$ ($\mu\text{ohm-cm}/$ atomic %)	χ^f/Ω (Vol. inc./vac. formation)	χ^m/Ω (Vol. inc./ vac. motion)	$(\chi^f + \chi^m)/\Omega$ (activation vol. for self-diffusion)
Au	7.2 ± 0.6^a	0.94 ± 0.09^a	0.98 ± 0.03^g 0.95 ± 0.1^h 0.97 ± 0.1^i	1.0^a	$1.5 \pm 0.3^{a,g}$ $1.8 \pm 0.6^{g,i}$ 2.4 ± 0.4^p	$0.45 \pm 0.10^{a,g,r}$ $0.57 \pm 0.05^{g,i}$	0.15 ± 0.02^s	$0.60 \pm 0.12^{a,g,r,s}$
Ag	1.7 ± 0.5^b	1.09 ± 0.10^b	1.10 ± 0.04^j 1.01 ± 0.03^k 1.06 ± 0.07^l	$1.5^{b,o}$	$1.3 \pm 0.7^{b,j}$	0.90^e
Al	9.0 ± 0.6^c	0.75 ± 0.07^c	0.79 ± 0.03^m 0.76 ± 0.04^n	2.2^c	$3^{q,l}$ $1.5^{e,l}$
Pb	$\leq 1.5^d$	$\geq 0.53^d$...	$1.5^{d,o}$	0.70^u 0.65^v

^a Present work.^b See reference 20.^c See reference 17.^d See reference 34.^e Including estimated possible systematic error.^f Including random errors only.^g See reference 2.^h See reference 40.ⁱ See reference 3.^j See reference 48.^k See reference 49.^l See reference 50.^m See reference 51.ⁿ See reference 41.^o Assumed value; see Sec. IV.B of text.^p See reference 10.^q See reference 45.^r See reference 6.^s See reference 7.^t See reference 58.^u See reference 56.^v See reference 57.

the measurements. (3) While the vacancy-type defects are undoubtedly created from dislocation sources, most of them are annihilated at stacking fault tetrahedra under the conditions of the calorimetric work, viz., quenched from about 800°C and annealed near 50°C.¹⁰ Upon such annihilation they release an amount of energy which is smaller than the standard formation energy in the lattice by an amount E_{sf} , where E_{sf} is the fault energy per destroyed defect. (4) It appears that a straight line of somewhat smaller slope than 0.97 ev/k would easily fit DeSorbo's data with equal precision; actually, DeSorbo's point at $9.07 \times 10^{-4}/^\circ\text{K}$ is misplotted in Fig. 3 of reference 3 at $8.97 \times 10^{-4}/^\circ\text{K}$. A smaller E^f would of course increase $\Delta E_T/E^f$. (5) Finally, an appreciable fraction of the defects, after quenching from above 820°C, may be bound up in a non-equilibrium distribution of divacancies or larger clusters. The energy release, per vacant lattice site, upon their annihilation is then decreased by an amount depending upon the magnitude of the binding energies of the clusters.

We note that the correction from factor (1) is uncertain in the absence of quenching rate experiments on foils. The correction from both factors (3) and (4) probably does not exceed 5%, if the stacking fault energy is less than 30 erg/cm². The correction from factor (5) is uncertain not only because the binding energies are not yet determined but also because the effective mobility and degree of clustering of the various defects during and after quenching is unknown.

The defect concentrations of Cotterill¹⁰ were deduced from measurements of stacking fault tetrahedron concentration and size in quenched and annealed foils. At temperatures below 900°C the results agree approximately with those of DeSorbo and have a stated probable error of 35%. The apparent disagreement at

900°C between the present work and the deductions of Cotterill is probably not larger than the sum of the respective estimated errors.

The calorimetric work of Pervakov and Khotkevich⁴ employed only 99.99% pure wires. Their quenching rate is not reported, but their residual electrical resistivity increases were substantially smaller than those typical of rapid quenching studies. A value of $E^f = 0.82$ ev was found. Their "most significant value" of defect concentration was $(7.6 \pm 1.0) \times 10^{-4}$ after quenching from 890°C. This value is shown near the top of Fig. 3 and is 250% larger than the present result. The disagreement is only slightly reduced by the use of a larger value of E^f . Such comparatively large concentrations have also been indirectly derived from other work using electrical resistivity and dilatometry,¹ and usually imply values of the formation energy which are anomalously low.

Table III shows a compilation of values of the defect concentration just below the melting temperature obtained by direct measurements of the present type on the four fcc metals so far examined. It is noteworthy that the largest concentration exceeds the smallest³⁴ by a factor of at least 6.

B. Monovacancy Abundance

All point defects contribute to $\Delta N/N$; and, therefore,

$$\Delta N/N = (c_{v1} + 2c_{v2} + 3c_{v3} + \cdots) - (c_{i1} + \cdots), \quad (4)$$

where c_{v1} , c_{v2} , and c_{v3} are the fractional concentrations of mono-, di-, and trivacancies, and c_{i1} is the concentration of interstitial atoms. Measurements of energy release during annealing of low-temperature irradiation damage in another noble metal, copper, lead to an estimate that the sum of interstitial and vacancy formation energies in

³⁴ R. Feder and A. S. Nowick, Phys. Rev. **109**, 1959 (1958).

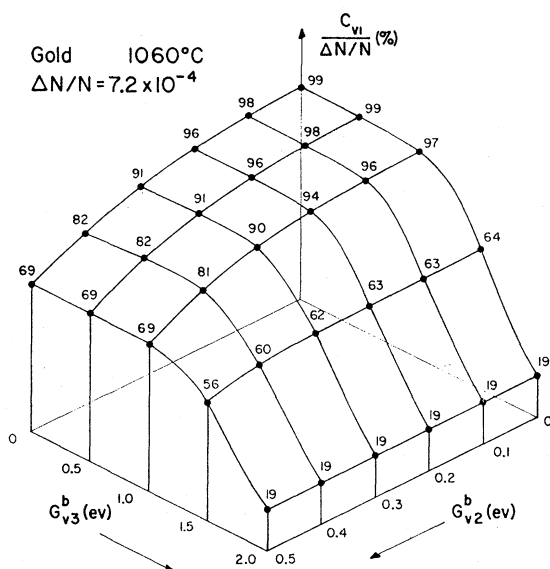


FIG. 4. Relative monovacancy abundance $c_{v1}/(\Delta N/N)$, as a function of divacancy and tetrahedral trivacancy binding energies G_{v2}^b and G_{v3}^b , in gold just below the melting temperature. It is probable that $G_{v2}^b < 0.4$ ev and $G_{v3}^b < 1.0$ ev.

copper is about 4 ev.³⁵ The expected equilibrium concentration of interstitial atoms is then negligible. It is probably also justifiable to neglect the equilibrium concentrations of vacancy aggregates formed from more than three vacancies.³⁶ Then the equilibrium concentrations of defects can be expressed in the following manner^{17,37}:

$$\begin{aligned} 3g_{v3} \exp(G_{v3}^b/kT)c_{v1}^3 \\ + 12 \exp(G_{v2}^b/kT)c_{v1}^2 + c_{v1} = \Delta N/N, \\ c_{v2} = 6c_{v1}^2 \exp(G_{v2}^b/kT), \\ c_{v3} = g_{v3}c_{v1}^3 \exp(G_{v3}^b/kT). \end{aligned} \quad (5)$$

The binding energies of the divacancy and trivacancy are denoted by G_{v2}^b and G_{v3}^b , respectively. The relations assume that the divacancy is a pair of nearest neighbor vacancies. If the trivacancy has tetrahedral symmetry, then $g_{v3} = 2$.

Equations (5) can be used to compute the main components of the defect population if $\Delta N/N$, G_{v2}^b , and G_{v3}^b are known. Unfortunately, the magnitudes of the binding energies are not firmly established. In order to indicate the trend of affairs the results have been computed for a wide range of G_{v2}^b and G_{v3}^b , with the assumption of tetrahedral trivacancies ($g_{v3} = 2$). The relative monovacancy abundance, as a function of binding

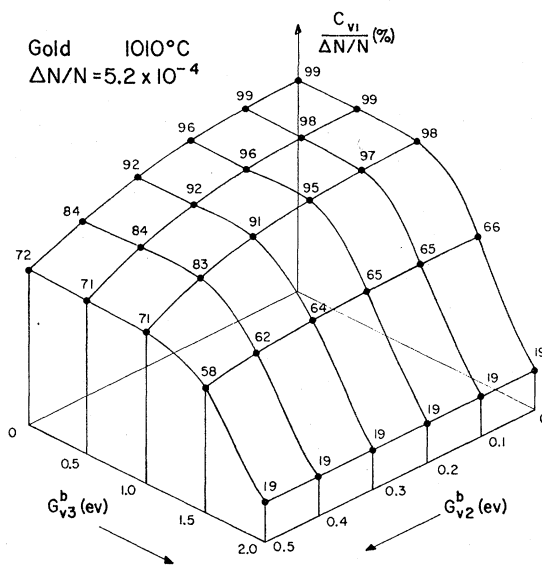


FIG. 5. Relative monovacancy abundance $c_{v1}/(\Delta N/N)$, as a function of divacancy and tetrahedral trivacancy binding energies G_{v2}^b and G_{v3}^b , in gold at 1010°C.

energies at a temperature just below the melting temperature, where $\Delta N/N = 7.2 \times 10^{-4}$, is shown in Fig. 4. Similar results for temperatures 50° and 100°C lower, where $\Delta N/N$ is 5.2×10^{-4} and 3.6×10^{-4} , respectively, are shown in Figs. 5 and 6.

A number of experimental and theoretical attempts have been made to determine G_{v2}^b . The largest proposed value has been 0.4 ev, while several investigators have proposed values less than 0.2 ev. We shall therefore as-

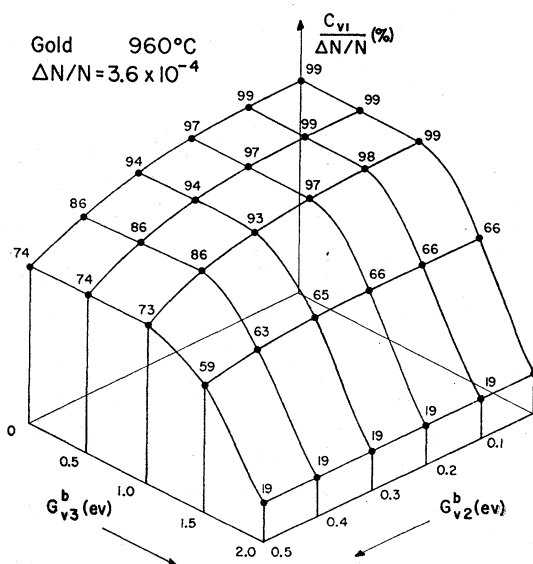


FIG. 6. Relative monovacancy abundance, $c_{v1}/(\Delta N/N)$, in gold at 960°C. Comparison with Figs. 4 and 5 shows the very weak temperature dependence of $c_{v1}/(\Delta N/N)$ for pairs of binding energies in the range of probable values. This allows the monovacancy formation energy to be determined from the slope of the line shown in Fig. 3.

³⁵ A. V. Granato and T. G. Nilan, Phys. Rev. Letters 6, 171 (1961).

³⁶ G. Schottky, Z. Physik 159, 584 (1960).

³⁷ These equations, as given in our previous paper on silver [see reference 20, Eq. (4)], contained an inadvertent error. The coefficient of the cubic term was erroneously written as 24 instead of its correct value of $3g_{v3}$ as above. However, all calculations presented in reference 20 were made using the correct coefficient $3g_{v3}$.

sume that $G_{v2}^b < 0.4$ ev. It is also reasonable to take $G_{v3}^b \approx 2G_{v2}^b$.³⁸ Under these conditions it is apparent from Figs. 4-6 that the equilibrium defects are predominantly monovacancies, the ratio $c_{v1}/(\Delta N/N)$ being larger than about 80% at these temperatures. In the following sections we shall obtain further information from the present results and the quenching experiments which is consistent with the above viewpoint.

C. Monovacancy Formation Energy and Entropy

Two methods can be used to evaluate the formation energy of the predominant monovacancy defects from the present equilibrium measurements. They are: (1) a direct examination of the temperature dependence of c_{v1} , which also leads to a direct estimate of the formation entropy, and (2) the adoption of a value of the formation entropy from theory combined with the most accurate value of c_{v1} at a known temperature.³⁴ We consider the methods in turn.

The equilibrium concentration of monovacancies is given from Eq. (2) by

$$c_{v1} = \exp(S_{v1}^f/k) \exp(-E_{v1}^f/kT), \quad (6)$$

and therefore, we require the temperature dependence of c_{v1} . It is readily shown that in view of our ignorance concerning the exact values of the vacancy binding energies that the temperature dependence of $\Delta N/N$ will serve just as well for present purposes when $G_{v2}^b < 0.4$ ev. The expected similar temperature dependences of c_{v1} and $\Delta N/N$ in the present case are demonstrated in Fig. 7, which shows the results of calculations of hypothetical $\Delta N/N$ values assuming values of c_{v1} in the range of the present results and values of G_{v2}^b of 0.0, 0.4, and 0.6 ev. Calculations based on these curves in the temperature range 1060°–900°C indicate that the apparent formation energy E_{v1}^f , derived from the $\Delta N/N$ curve exceeds E_{v1}^f by only 0.095 ev in the extreme case when $G_{v2}^b = 0.4$ ev. We therefore conclude from Figs. 3 and 7 that E_{v1}^f lies between the limits 0.94 ± 0.09 ev.

The derived value of the monovacancy entropy of formation has only a weak dependence upon the values of the binding energies. For example, when $E_{v1}^f = 0.94$ ev and $G_{v2}^b = G_{v3}^b = 0$, one finds $S_{v1}^f/k = 1.0$, while for $G_{v2}^b = 0.3$ ev and $G_{v3}^b = 0.6$ to 0.9 ev one finds S_{v1}^f/k slightly less than 0.9.

A variety of calculations have given theoretical values of S_{v1}^f suitable for use in method (2).³⁹ A reasonable assumption is $S_{v1}^f/k = 1.5 \pm 0.5$. Application of Eq. (6) then yields a value of E_{v1}^f . For $G_{v2}^b = G_{v3}^b = 0$, $c_{v1} = (7.2 \pm 0.6) \times 10^{-4}$ at 1333°K, which gives $E_{v1}^f = 1.00 \pm 0.11$ ev. For $G_{v2}^b = 0.3$ ev and $G_{v3}^b = 0.6$ to 0.9 ev, $c_{v1} = 6.5 \times 10^{-4}$ at the same temperature, which gives $E_{v1}^f = 1.01 \pm 0.11$ ev. These values are not inconsistent

³⁸ We note that the calculations are not sensitive to the value of G_{v3}^b in this range.

³⁹ See the brief discussion in reference 20.

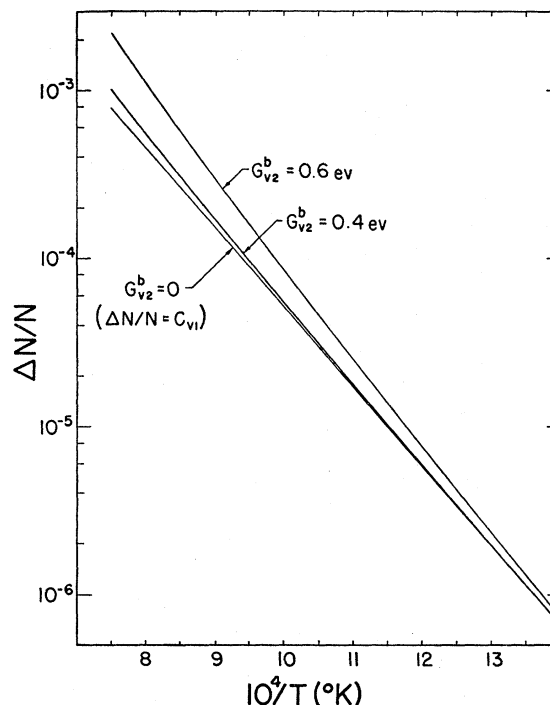


FIG. 7. Hypothetical temperature dependence of $\Delta N/N$ for different divacancy binding energies G_{v2}^b . Values have been calculated by using Eq. (5) and assuming $c_{v1} = \exp(1.0) \exp(-0.94 \text{ ev}/kT)$ and $G_{v3}^b = 2G_{v2}^b$.³⁸ If $G_{v2}^b = 0$, the divacancy concentrations would be negligible, and $\Delta N/N = c_{v1}$. If $G_{v2}^b = 0.4$ ev, a small but significant divacancy concentration would be present at the higher temperatures. If $G_{v2}^b = 0.6$ ev, the divacancy concentration would be comparable to the monovacancy concentration over most of the temperature range.

with the results obtained by method (1) when all uncertainties are considered.

In line with our expectation that G_{v2}^b is comparatively small, we take $E_{v1}^f = 0.94$ ev and $S_{v1}^f/k = 1.0$ as best values from the present equilibrium measurements. Some further support for these values is given in the following section.

D. Comparison with Quenching Results

The work of Bauerle and Koehler² showed that for wires quenched at 3×10^4 deg/sec the quenched-in resistivity followed the relation

$$\Delta \rho = [(4.9 \pm 1.0) \times 10^{-4} \text{ ohm-cm}] \times \exp[-(0.98 \pm 0.03 \text{ ev})/kT_Q], \quad (7)$$

where T_Q is the temperature previous to quenching. The published curve of $\ln \Delta \rho$ versus $1/T_Q$ appears straight without any detectable systematic curvature. According to the calculated curves in Fig. 7 a noticeable positive curvature should have been present if $G_{v2}^b > 0.4$ ev and if any vacancy aggregation occurring during quenching did not appreciably alter the electron scattering cross section per vacant lattice site. Losses during the quenching process may of course lead to a negative

curvature. However, the work of Bradshaw and Pearson on gold,⁴⁰ aluminum,⁴¹ and platinum⁴² has shown that apparently straightforward calculations of vacancy migration and aggregation during quenching¹⁵ may be misleading. For example, even a knowledge of such properties as the quenching rate, E_{v1}^m and G_{v2}^b does not permit one to predict the maximum temperature T_Q , to which the linearity of $\ln\Delta\rho$ versus T_Q^{-1} holds.

For quenching temperatures T_Q , in the interval 450°–1000°C, the $\Delta\rho$ obtained by Bauerle and Koehler varied by nearly a factor 10^3 ; this large variation obtained would tend to promote confidence that (1) the equilibrium defect concentrations were being retained by the quenching process, and (2) the observed slope of $\ln\Delta\rho$ versus $1/kT_Q$ corresponded to the formation energy of the defects.

The annealing behavior of the wires studied by Bauerle and Koehler² depended markedly upon T_Q . For T_Q below 700°C the time decay of $\Delta\rho$ was essentially a simple exponential, and the residual amount remaining after a long anneal near 50°C was less than 1%. This behavior is consistent with the simple migration of monovacancies to fixed sinks. Such an interpretation is supported by the measured value of the migration energy, $E^m = (0.82 \pm 0.05)$ ev, which is in agreement with the difference $Q - E_{v1}^f$ where $Q = (1.81 \pm 0.02)$ ev is the measured activation energy for self-diffusion.⁴³ We note that the presence of only monovacancies for T_Q near and below 700°C is also consistent with $G_{v2}^b < 0.4$ in Fig. 7. For T_Q larger than 850°C the decay during annealing was much more rapid and showed an inflection point; the residual amount was about 10%. This residual 10% $\Delta\rho$ annealed between 500° and 800°C; it is clearly to be associated with the stacking fault tetrahedra observed in thinned foils quenched from above 800°C by Silcox and Hirsch⁹ and by Cotterill.⁴⁴

Bauerle and Koehler also report the following puzzling result. Doubling the quenching rate produced a 15 to 20% increase in $\Delta\rho$ at all T_Q 's used (in the narrower range 600° to 900°C). This curious phenomenon is also present if the work of independent investigators is compared.⁴⁵ A common value of E^f may be indicated but the magnitude of $\Delta\rho$, for a selected T_Q , is, in general, different for slightly different experimental conditions (quenching rate, wire diameter, quenching medium, possible deformation, and so on).

In the absence of any comprehensive study of the influence of these factors upon the magnitude of the pre-exponential factor in Eq. (7) the assumption will be made that Eq. (7) represents, within the error given, the

contribution to electrical resistivity from the equilibrium vacancy concentrations in gold. No investigators using rapid quenching have reported any larger contributions. Further, the work of Cotterill,¹⁰ who observes only a small concentration of "black spot defects" (about 25-Å diameter) and no tetrahedra, immediately after quenching, and who argues that such defects contribute less than 10% to $\Delta\rho$, suggests that the assumption is valid.

The formation energy given in Eq. (7) should represent the monovacancy energy quite closely even if G_{v2}^b is as large as 0.4 ev. According to Fig. 7 a value of $G_{v2}^b = 0.4$ ev will produce an overestimate of E_{v1}^f of only about 0.035 ev when the calculation is made over the whole temperature range 450°–900°C. In summary it appears that the values of E_{v1}^f derived from the present equilibrium measurements and the Bauerle and Koehler quenching experiments are in satisfactory agreement.

A great many additional experimental and derived values for E^f in gold have been published. They will not be collected here.^{1,46} However, the values can be placed in two groups as follows: Group I containing more than nine values in the range 0.94 to 1.02 ev obtained from rapid quenching studies; and Group II containing more than six values in the range 0.62 to 0.82 ev. Indirectly derived values from various extrapolation schemes, e.g., extrapolation of lattice electrical resistivity or thermal expansion, have generally given values in Group II.⁴⁷ The difficulties involved in extrapolation methods have been stressed by the writers previously.⁴⁵

Table III shows the good agreement between the present value of E_{v1}^f for gold and values from Group I.^{2,3,40} The table also contains similar comparisons for the metals Ag^{48–50} and Al.^{41,51}

E. Monovacancy Resistivity

The previous discussion allows an evaluation of the monovacancy resistivity. For $T_Q = 900^\circ\text{C}$, Bauerle and Koehler² obtained $\Delta\rho = 3.5 \times 10^{-8}$ ohm-cm. This resistivity increment can be expressed as

$$\Delta\rho = \rho_{v1}c_{v1} + \rho_{v2}c_{v2} + \rho_{v3}c_{v3} + \dots,$$

where the ρ_{vj} are constants which may depend weakly upon temperature. Now in Sec. V.D it has been argued that $c_{v1} \gtrsim 5c_{v2}$ and $c_{v1} \gtrsim 10c_{v3}$ in equilibrium and also probably immediately after rapid quenching from 900°C. Further, it is probable that in the noble metals

⁴⁰ F. J. Bradshaw and S. Pearson, *Phil. Mag.* **2**, 370 (1957).
⁴¹ F. J. Bradshaw and S. Pearson, *Phil. Mag.* **2**, 570 (1957).
⁴² F. J. Bradshaw and S. Pearson, *Phil. Mag.* **1**, 812 (1956).

⁴³ S. J. Makin, A. H. Rowe, and A. D. LeClaire, *Proc. Phys. Soc. (London)* **B70**, 545 (1957).
⁴⁴ See reference 10: Cotterill observes the annealing temperature to be 650°C in 99.999% purity foil.
⁴⁵ R. O. Simmons and R. W. Balluffi, *Phys. Rev.* **117**, 62 (1960).

⁴⁶ A recent compilation which also includes many controversial values for properties of other defects is W. Schüle, A. Seeger, F. Ramsteiner, D. Schumacher, and K. King, *Z. Naturforsch.* **16a**, 323 (1961).
⁴⁷ S. D. Gertsriken and B. F. Slyusar, *Fiz. Metal. i Metalloved. Akad. Nauk S.S.S.R., Ural. Filial* **6**, 1061 (1958) [translation; *Phys. of Metals and Metallography* **6**, 1061 (1959)].

⁴⁸ M. Doyama and J. S. Koehler, *Phys. Rev.* **119**, 939 (1960).
⁴⁹ S. D. Gertsriken and N. N. Novikov, *Fiz. Metal. i Metalloved. Akad. Nauk S.S.S.R., Ural. Filial* **9**, 224 (1960) [translation; *Phys. of Metals and Metallography* **9**, No. 2, 54 (1960)].
⁵⁰ Y. Quere, *Compt. rend.* **251**, 367 (1960).
⁵¹ W. DeSorbo and D. Turnbull, *Acta Met.* **7**, 83 (1959).

$\rho_{v1} \approx \frac{1}{2}\rho_{v2} \approx \frac{1}{3}\rho_{v3}$ within 10 to 20%.⁵² Then

$$\Delta\rho \approx \rho_{v1}(c_{v1} + 2c_{v2} + 3c_{v3} + \dots) = \rho_{v1}\Delta N/N.$$

The appropriate concentration value to use is therefore the total one, which is found from the present measurements to be $\Delta N/N = 2.4 \times 10^{-4}$ at 900°C. Therefore,

$$\rho_{v1} = (1.5 \pm 0.3) \mu\text{ohm-cm/at.}\% \text{ vacancies.} \quad (8)$$

The assigned uncertainty was obtained not only from a consideration of the above approximations but also from the individual errors in the measurement of $\Delta\rho$ and of $\Delta N/N$ and from a comparison of the results summarized in Eqs. (3) and (7).

This value of vacancy resistivity is in good agreement with published theoretical estimates.⁵³ It is compared to other experimentally derived values in Table III. A somewhat larger value, stated to be a lower limit, was obtained in the comparison study of Cotterill,¹⁰ whose derived concentration values are shown in Fig. 3. The apparent disagreement is not considered to be serious, in view of the difficulties inherent in his comparison studies and the many assumptions required in their analysis. The derived value of DeSorbo³ was obtained using his concentrations shown on Fig. 3 together with a somewhat questionable correction for differences in quenching rate applied to Eq. (7).

F. Monovacancy Volume Expansion

Bauerle and Koehler² report measurements of relative length contraction during annealing, for three quenches having $T_Q > 850^\circ\text{C}$ and one quench having T_Q about 700°C . Essentially the same volume change is to be expected per vacancy annihilated whether the vacancy migrates to a dislocation sink or it participates in the formation of a stacking fault tetrahedron. A simple mean value for the proportionality factor between the resistivity decrease and the fractional volume decrease $\Delta V/V$ can then be adopted. It is

$$\Delta\rho/(\Delta V/V) = 3.3 \times 10^{-4} \text{ ohm-cm,} \quad (9)$$

if the dimensional changes upon annealing of the polycrystalline wires are isotropic.

Length contraction during annealing of polycrystalline wires has also been studied by Takamura.⁶ An extrapolation to small wire diameter yields for the total

contraction, assumed isotropic, a result

$$\Delta V_T/V = 1.4 \exp(-0.98 \text{ eV}/kT_Q). \quad (10)$$

The volume expansion upon formation of a vacancy, χ' , can then be derived in two ways. (1) The ratio of resistivity to relative volume change upon annealing, Eq. (9), can be combined with Eq. (8). (2) The total volume contraction upon annealing, Eq. (10), can be compared to the equilibrium $\Delta N/N$ values shown in Fig. 3. Both methods yield the same result:

$$\chi'/\Omega = 0.45 \pm 0.10. \quad (11)$$

where $\Omega = a^3/4$ is the atomic volume. Both methods employ total defect concentrations and depend upon the assumptions discussed in Sec. V. D. The estimate of error, while believed to be reliable, is therefore somewhat uncertain; a more direct experimental determination would be very desirable.

Theoretical estimates of the volume change due to the monovacancy have been made primarily for copper,^{54,55} and therefore cannot be directly compared to Eq. (11). One estimate⁵⁵ is very near the value found for gold. The derived value of DeSorbo, shown in Table III, is probably somewhat large, for the same reasons that his ρ_{v1} may be.

Emrick has deduced a value for the volume change upon motion of a vacancy in gold from studies of the pressure dependence of the annealing of quenched wires. It is $\chi^m/\Omega = 0.15 \pm 0.02$. The activation volume for self-diffusion is then given as $\chi^m + \chi' = 0.60$ atomic volume. Unfortunately, this quantity has not been determined experimentally for gold; however, this value is near the value 0.70 for the fcc metal lead, as determined from studies of the pressure dependence of self-diffusion.^{56,57} Only a preliminary report of similar work on silver has been made.⁵⁸

Values of monovacancy properties derived from experiments have been collected in Table III, for the cases in which equilibrium vacancy concentrations have been measured.

ACKNOWLEDGMENT

The writers wish to thank Anthony J. Schaeffer for his aid in carrying out the experimental portion of the present work.

⁵⁴ A. Seeger and E. Mann, *J. Phys. Chem. Solids* **12**, 326 (1960).

⁵⁵ K. H. Bennemann and L. Tewordt, *Z. Naturforsch.* **15a**, 772 (1960).

⁵⁶ N. H. Nachtrieb, H. A. Riesing, and S. A. Rice, *J. Chem. Phys.* **31**, 135 (1959).

⁵⁷ J. B. Hudson, in *Progress in Very High Pressure Research* (Wiley & Sons, Inc., New York, 1961), p. 269.

⁵⁸ C. T. Tomizuka, in *Progress in Very High Pressure Research* (Wiley & Sons, Inc., New York, 1961), p. 266.

⁵² A. Seeger and H. Bross, *J. Phys. Chem. Solids* **6**, 324 (1958).

⁵³ Such estimates are reviewed by F. Blatt, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4, p. 199.