Effect of Pressure on Quenched-In Electrical Resistance in Gold and Aluminum*†

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The effect of pressures up to 6 kbar on the electrical resistance quenched into gold and aluminum at various linear quench rates has been measured. Formation volumes of 6.8 ± 0.4 and 6.38 ± 0.15 cm³/mole, respectively, are inferred. Agreement with earlier measurements in gold is good when they are corrected for the pressure coefficient of resistance. The value for aluminum supports earlier values obtained by other techniques. There is also evidence that dislocations are not sinks for the majority of the vacancies during the quench.

I. INTRODUCTION

DIFFUSION theory shows that the activation energy for self-diffusion Q is the sum of the formation energy E_f of the defect responsible for diffusion and of its motional energy E_m. For many fcc metals, where the single-vacancy mechanism is responsible for self-diffusion, it has been experimentally verified by independent measurement of each quantity that $Q = E_f^1 + E_m^1$, where the superscript indicates single-vacancy values.[1] By the same theory, the activation volume for self-diffusion ΔV_{act} should equal the sum of the formation volume ΔV_f and the motional volume ΔV_m of the defects responsible for diffusion. ΔV_f is interpreted as the volume change of the crystal when a mole of defects is present and ΔV_m is the volume change when a mole of defects is in the activated state, i.e., halfway between initial and final equilibrium states.

Only one experimental test of the volume relationship has been made. Huebener and Homan[2] and Grimes[3] have determined ΔV_f for gold, Emrick[4] ΔV_m, and Dickerson, Lowell, and Tomizuka[5] and Beyeler and Adda[6] ΔV_{act}. The agreement is within experimental error. More recently Bourassa, Lazarus, and Blackburn[7] (BLB) have determined ΔV_f from an interpretation of pressure and temperature effects on resistivity and thermoelectric power in gold. Their value, while somewhat larger than the quenching value, agrees within experimental errors.

Another important measurement by BLB[7] was the pressure coefficient of resistivity of aluminum and gold

at high temperatures. The earlier data of Bridgman[8] did not extend much above room temperature. Although these coefficients are pressure-independent, they do depend on temperature. The quench temperatures in the previous ΔV_f measurements were determined from the room-temperature coefficients, thereby introducing a pressure-dependent error in the quench temperature. The quenching experiments also assumed either no vacancy loss during quench or a pressure-independent loss. Flynn, Bass, and Lazarus[9] (FBL), and Kino and Koehler[10] have constructed theories for vacancy loss for constant quenching rates. A recently developed temperature controller[11] permits linear quenches at any rate up to the limit imposed by the specimen environment. We therefore have remeasured ΔV_f for gold and measured ΔV_f for aluminum taking into account these new results. The pressure dependence of the vacancy loss also permits a test of some of the models for the loss during quench.

II. THEORY

The earlier papers[2–4] give more detailed thermodynamic arguments for inferring the defect formation volume ΔV_f. One finds that the equilibrium vacancy concentration is given by

$$c(T) = c_0 e^{-\Delta G_f/kT}, \qquad (1)$$

where ΔG_f is the Gibb's free energy to form a defect. The volume of formation is thermodynamically related to ΔG_f by

$$\Delta V_f = (\partial \Delta G_f / \partial P)_T. \qquad (2)$$

If we assume that the pressure effect on c_0 is small compared with experimental error and that the quenched-in resistance $\Delta R/R_0$ is proportional to the vacancy concentration, we then find

$$\Delta V_f = -kT_Q \left(\frac{\partial \ln(\Delta R/R_0)}{\partial P} \right)_{T_Q}. \qquad (3)$$

[1] See, for example, the reviews in *Lattice Defects in Quenched Metals*, edited by R. M. J. Cotterill, M. Doyama, J. J. Jackson, and M. Meshii (Academic Press Inc., New York, 1965).

[2] R. P. Huebener and C. G. Homan, Phys. Rev. 129, 1162 (1963).

[3] H. H. Grimes, J. Phys. Chem. Solids 26, 509 (1965).

[4] R. M. Emrick, Phys. Rev. 122, 1720 (1961).

[5] R. H. Dickerson, R. C. Lowell, and C. T. Tomizuka, Phys. Rev. 137, 613 (1965).

[6] M. Beyeler and Y. Adda, J. Phys. (Paris) 29, 345 (1968).

[7] R. R. Bourassa, D. Lazarus, and D. A. Blackburn, Phys. Rev. 165, 853 (1968).

[8] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 52, 573 (1917).

[9] C. P. Flynn, J. Bass, and D. Lazarus, Phil. Mag. 11, 521 (1965).

[10] T. Kino and J. S. Koehler, Phys. Rev. 162, 632 (1967).

[11] R. M. Emrick and D. E. McDonald, Rev. Sci. Instr. 40, 82 (1969).

A measurement of $\Delta R/R_0$ for infinite quench rate from a fixed temperature as a function of pressure can then be interpreted in terms of the formation volume of the defect.

A difficulty arises from the fact that for finite quench rates some of the defects have time to migrate to sinks where they are annihilated. FBL[9] recognized that the driving force for vacancy anneal during quench depends on the vacancy supersaturation at the instantaneous temperature rather than at the final temperature. By assuming that the vacancies anneal by a single process to a fixed, random distribution of sinks they showed that the fractional vacancy loss depends on $D_Q T_Q \tau_Q$, where D_Q is the diffusion coefficient at the quench temperature T_Q, and τ_Q is the rate parameter in the presumed linear quench $T(t) = T_Q(1 - t/\tau_Q)$. By keeping T_Q and the quench pressure P fixed and varying τ_Q, we have a means of extrapolating to infinite quench rate to determine the equilibrium concentration at T_Q and P.

Kino and Koehler[10] extended the calculations to consider the details of the dependence on various sink mechanisms. For all mechanisms considered, the fractional vacancy loss was linear in τ_Q. Thus for small fractional losses, even if several mechanisms are operating simultaneously, the linear extrapolation to infinite quench rate should be appropriate.

III. EXPERIMENTAL

A. Gold Specimens

The gold specimens were fabricated from 0.004-in.-diam wire drawn by Cominco American, Inc., Spokane, Wash., from nominally 99.9999% pure ingots. Potential leads were 0.0006-in.-diam 99.99% gold wire supplied by Sigmund Cohn Corp., Mount Vernon, N. Y. Both specimen and dummy were given a 30-min 900°C air anneal after cleaning with acetone. After insertion into the pressure vessel, tank pressure argon was introduced and both specimen and dummy were annealed at 800°C for 10 min, 500°C for 5 min, and 300°C for 15 min. The latter treatment was given the specimen before each quench to obtain a reproducible resistance base as discussed by Bass.[12] This procedure was effective, the resistance increase between quenches being less than 0.6 $\mu\Omega$ when the total quenched in was 10–30 $\mu\Omega$. The gold temperature scale used was that of Northrup[13] and Meechan and Eggleston.[14]

B. Aluminum Specimens

The aluminum specimens were made from 0.004-in.-diam wire of nominal 99.999% purity supplied by the Sigmund Cohn Corp. The wires were etched in a phosphoric- and chromic-acid mixture and rinsed in
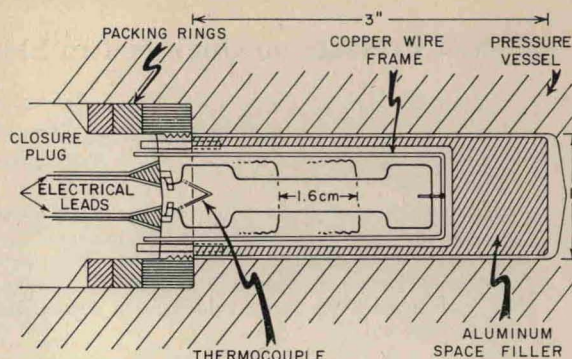

FIG. 1. Schematic diagram of specimen and dummy mounted in pressure vessel. The closure plug has a total of eight electrical leads.

distilled water. Potential leads were also the 0.0006-in.-diam 99.99% gold, since small diameter aluminum leads could never be spot-welded successfully. The initial anneals were 30 min at 550°C and 45 min each at 300 and 100°C. The last two were subsequently reduced to 20 min each. The resistance baseline shifts were somewhat larger than for gold, but reproducible results were obtained after shifts which varied from 0.6 to 3.0 $\mu\Omega$. Data after shifts in excess of the latter value were excluded. The aluminum temperature scale used was that of Simmons and Balluffi.[15]

C. Specimen Shape

The position of the leads was adjusted before spot-welding to minimize the difference in resistance between specimen and dummy. Small temperature differences between specimen and dummy had a negligible effect on the measurement of quenched-in resistance ΔR. ΔR was measured by the standard bridge techniques to about ± 0.1 $\mu\Omega$,[16–18] using a Rubicon 6-dial potentiometer and photoelectric galvanometer. The measuring current was monitored to 0.05000 ± 0.00002 A by use of an L&N K3 potentiometer across a 1-Ω standard in series with the specimen.

The total specimen length was about 6 cm and the gauge region about 1.6 cm long, as shown in Fig. 1. This gauge region was well within the uniform temperature region observed visually in gold at 900°C. Since the quenches were made at 720°C and less and since the pressure gas would tend to reduce the importance of conduction along the wire, the temperature gradients in the gauge region were assumed to be small. This assumption was confirmed by spot-welding two extra potential leads in the gauge region of a test specimen. The relative voltage drops across the three regions defined by the four leads remained constant to

[12] J. Bass, dissertation, University of Illinois, 1964 (unpublished).
[13] E. F. Northrup, J. Franklin Inst. 177, 287 (1914).
[14] C. J. Meechan and R. N. Eggleston, Acta Met. 2, 680 (1954).

[15] R. O. Simmons and R. W. Balluffi, Phys. Rev. 117, 62 (1960).
[16] J. W. Kauffman and J. S. Koehler, Phys. Rev. 88, 149 (1952).
[17] J. E. Bauerle and J. S. Koehler, Phys. Rev. 107, 1493 (1957).
[18] R. M. Emrick, U. S. Air Force Office of Scientific Research Technical Report No. 2581 (unpublished).
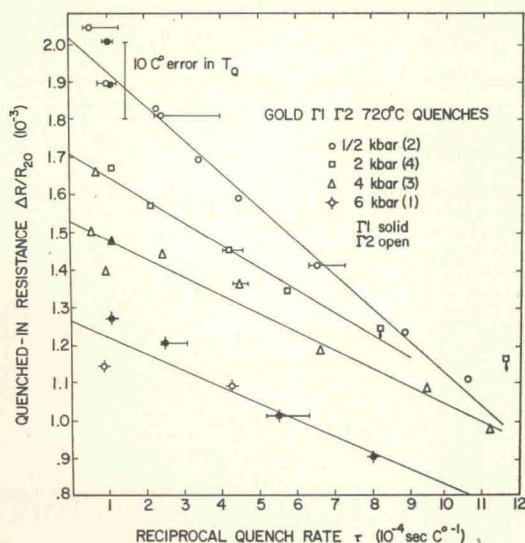
FIG. 2. Isobars of quenched-in resistance versus reciprocal quench rate for high-temperature quenches of gold. Numbers in parentheses indicate sequence in which isobars were made.

three figures from room temperature to beyond the quench temperature.

D. Pressure Apparatus

The specimen frame was inserted in a rectangular slot in a 1-in.-diam aluminum cylinder. The cylinder minimized the dead volume in the pressure vessel and helped minimize temperature gradients. The pressure system was a standard gas system with a Harwood intensifier operated with dry piston packings and a 1:1 separator in the priming line to minimize the possibility of oil entering the system. Pressure was measured by a manganin gauge calibrated against the freezing pressure of mercury. The pressure medium was ultra-high purity argon for most series of quenches. However, no differences in results could be attributed to the use of commercial grade argon on several runs.

E. Experimental Procedure

Since it was difficult and undesirable to immerse the specimen plug in a temperature bath, the specimen resistance was measured in the pressure vessel at atmospheric pressure and temperature. Specimen temperature was determined by the thermocouple on the plug (Fig. 1) which had been calibrated against an ASTM thermometer. This value of resistance was then used as the base for the temperature scale. (The thermocouple was not used to determine the quench temperature.) Since the thermocouple was not in direct contact with the specimen it is possible that the temperature scale from one specimen to the next varied by $\pm 5°C$ at T_Q. Thus direct comparison of values of ΔR for a given P and indicated T_Q from one specimen with those of another is difficult. Fortunately,

the specimen remains in place with no further handling once it is in the vessel. An entire series of quenches at different rates and pressures can be performed on a single specimen. It is therefore possible to do the entire series without affecting dislocation densities due to mechanical strains. Thermal strains are also minimized since the maximum quench rate was 2×10^4 C°/sec.

After annealing, the resistance base $\delta R_b{}^4$ was measured at bottle gas pressure with both current directions to minimize the effect of thermal emf's. The system was then pumped to the quench pressure. The specimen was heated slowly to T_Q by use of the temperature controller. T_Q was determined by measuring the specimen voltage with an L&N K3 potentiometer and specimen current with a Weston Model 931 ammeter which was calibrated against a 1-Ω resistance standard. Specimen resistance at T_Q was calculated using the BLB data. A Tektronix 555 Dual-Beam oscilloscope was triggered after the K3 potentiometer output indicated a stable temperature had been attained. The scope-delayed trigger started the linear ramp which quenched the specimen while the specimen voltage and current were recorded on Polaroid film. Trace intensity was modulated by pulses from a Tektronix Type 184 Time-Mark generator operating into the z-axis inputs of the 555. This procedure eliminated errors due to variations in sweep speed between the two beams. The photographic traces could then be analyzed to determine quench rates.[11]

Variations in T_Q due to turbulence of the pressure gas are the chief source of error. It is necessary for the controller to sense the resistance of the entire specimen length. The gauge length can therefore fluctuate as much as $\pm 15°C$ while the *average* temperature of the
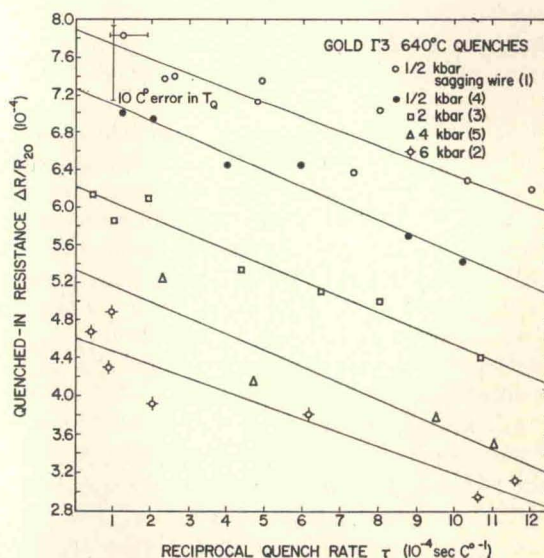

FIG. 3. Isobars of quenched-in resistance versus reciprocal quench rate for low-temperature gold quenches. Numbers in parentheses indicate sequence in which isobars were made. After taking isobar (1), it was discovered that the specimen sagged during the interquench anneals.

entire specimen remains constant. Small pressure leaks had a dramatic effect on temperature stability, presumably because they introduced currents in the high-pressure gas. Errors in reading the films led to an uncertainty of $\pm 10°C$ in measuring temperature. When the quench temperature indicated by the film was more than 10°C away from the desired value, the results of the quench were discarded.

The resistance after quench was measured immediately after the pressure had been released, typically within 8 min after quench and never more than 15 min. A single measurement (the average over two current directions) could be taken within 6 min after quench. Occasionally measurements were taken over a period of $\frac{1}{2}$ h. No resistance annealing could be detected. For the gold specimens the vessel was at ambient (22–25°C), while for aluminum the vessel was packed in dry ice (about −80°C). Although there was a diurnal variation in internal vessel temperature of about 3°C, no effects could be attributed to it.

Quenches were made at various rates at a given pressure. The sequence of quenches mixed fast and slow rates to reduce the effects of a possible change in specimen purity with use. The sequence of pressures was also varied for the same reason.

IV. RESULTS

A. Gold

Figures 2–4 are isobars of $\Delta R/R_{20}$ versus τ for gold specimens $\Gamma 2$, $\Gamma 3$, and $\Gamma 4$. Four isobars were also made with specimen $\Gamma 2$ for 640°C quenches. Note that τ is the reciprocal quench rate $\dot{T}^{-1}$ and not τ_Q as discussed in the theory section. They are related by $\tau_Q = T_Q \tau$. Measurement errors in $\Delta R/R_{20}$ are smaller than the symbols. An error of 10°C in quench temperature is indicated by the vertical bars for $E_F = 0.98$ eV, $P = \frac{1}{2}$ kbar, and $\tau = 1 \times 10^{-4}$ sec/°C. That is, a 10°C error in quench temperature produces a change of about 13% in the equilibrium concentration. Except where noted by error bars, the quench rates are quite linear to at least 500°C below the quench temperature. Occasionally the quench rate would change after the first 100 to 200°C drop in temperature. The range in slopes is indicated by error bars but the point is weighted in favor of the initial slope. In Fig. 3, two $\frac{1}{2}$-kbar isobars are shown. During the first $\frac{1}{2}$-kbar run it was noted that a large (2.5-$\mu\Omega$) baseline shift occurred after each anneal. The specimen was removed from the vessel and found to have sagged excessively. A 0.0006-in. gold wire support was looped under the specimen to lift it back to a nearly horizontal position. It was then given another 25-min 900°C air anneal before replacing in the vessel. The other four isobars were then taken in the order indicated. Specimen $\Gamma 2$ had no such support, but it neither sagged nor showed the large baseline shift. As a precaution, $\Gamma 4$ was also made with
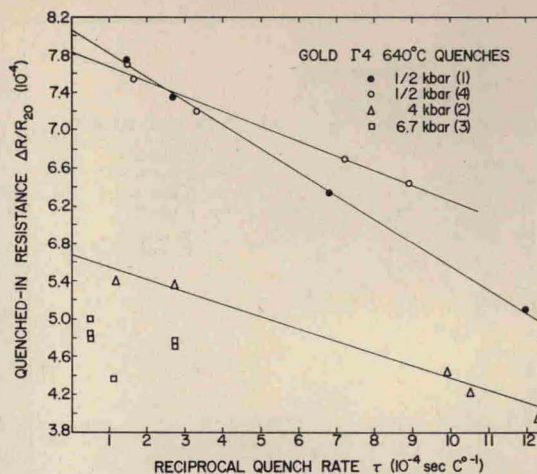

FIG. 4. Isobars of quenched-in resistance versus reciprocal quench rate. Numbers in parentheses indicate sequence in which isobars were made.

a support. The support had no visible effect on temperature uniformity at 900°C in air on either $\Gamma 3$ or $\Gamma 4$. Despite the baseline shift, the first $\frac{1}{2}$-kbar isobar is a straight line. Thus, a straight line alone cannot be taken as evidence of good data. The baseline shift was presumably caused by the sag of the specimen during anneal. Whether the resistance change was due to a change in dislocation density or specimen dimensions could not be determined.

At 6 kbar it was possible to get quench rates in excess of 1×10^4°C sec^{-1}. Specimen $\Gamma 4$ was used to determine whether or not the slope for the 1×10^4 to 1×10^3°C sec^{-1} isobars continued to the higher quench rates. These rates, $\dot{T} > 10^4$°C sec^{-1}, are the ones typical for quenches into liquids. The heating current decreased so rapidly to produce these high quench rates that the voltage signals were too small to be measured with any degree of accuracy. The ramp speed was found to be linear in the time-constant resistor over a wide range, so the fast quench rates were inferred from the ramp control potentiometer setting. The pressure system was leaking badly at 6.7 kbar, so the full isobar was not traced out. Nonetheless, it is seen to be consistent with the 4-kbar isobar, even for the fastest quenches.

Another interesting result from this specimen is the decrease in slope of the $\frac{1}{2}$-kbar isobar after the 6.7-kbar run. The intercepts agree within 3% but the slope decreases by a factor of 1.6. Further experiments are being made in an attempt to determine the behavior of the sinks under pressure. This result does indicate that our extrapolated values are nearly independent of sink concentration. This is as expected unless the dominant sink is an impurity which has a large vacancy-impurity binding energy.

In Fig. 5 the intercepts are plotted as a function of pressure. The 640°C data do not superpose because of the variation in absolute temperature scale from one specimen to the next as discussed in Sec. III E. The
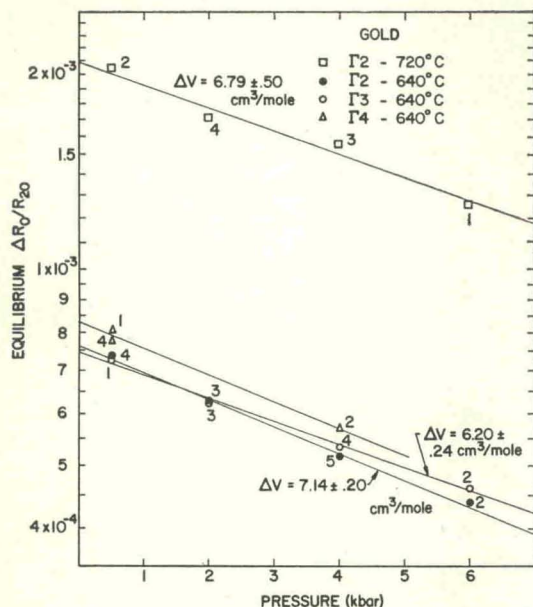
FIG. 5. Extrapolated relative equilibrium vacancy concentration at a given temperature as a function of pressure in gold. Numbers by points show sequence in which points were taken on a given isotherm.

activation volume corresponding to the least-squares straight line along with the least-squares error is shown for each specimen. Weighting each value by the reciprocal of the least-squares error (and taking the error of $\Gamma4$ to be ±1 cm³/mole since so few points are involved), an average value for ΔV_f is found to be

$$\Delta V_f = 6.8 \pm 0.4 \text{ cm}^3/\text{mole.}$$

This is $0.65 \ V_m$, where V_m is the 640°C molar volume of gold.

B. Aluminum

Of 19 aluminum specimens constructed and placed in the pressure vessel, only two remained intact long enough to obtain data at more than two pressures. Of these, the results for Al 14 are shown in Fig. 6. The pre-quench temperature stability as indicated by the K3 potentiometer was better than ±1°C. This stability is reflected in the reproducibility and small scatter of the data. The intercepts of Fig. 6 are plotted in Fig. 7. The results for the other specimens, where more than one isobar was obtained, were consistent with the results for Al 14. If there was any trend in these other data, it was toward a smaller formation volume. However, in those cases there was a large baseline shift between quenches so that those results cannot be given much consideration. None of the aluminum specimens was observed to sag as in the case of gold. Some did appear to discolor, however, which was not the case for gold. The resistance base shift in aluminum may therefore be due to impurities introduced during the anneals.

Unfortunately it has not been possible to measure the residual resistivity of the specimens after the series of quenches.

Quench rates were constant to below 0°C for the aluminum specimens. High-pressure fast quenches were also found to be consistent with the slower quenches. Several quenches were also made from a lower temperature (375°C) and were in agreement with, but had larger error than, Al 14. Thus, for aluminum

$$\Delta V_f = 6.38 \pm 0.15 \text{ cm}^3/\text{mole.}$$

The error indicates only the least-squares fit to the plot of the intercepts versus pressure. The value is $0.62 \ V_m$, where V_m is the 420°C molar volume of aluminum.

V. DISCUSSION

A. Gold

1. Formation Volumes

Several formation volumes for vacancies in gold have been reported. They have been discussed in the quenching papers[2,3] and the BLB paper.[7] All are in fair agreement within their respective experimental errors. The present value agrees with the BLB value within the stated errors but is considerably higher than the earlier quenching values. There are several reasons for this discrepancy.

The earlier quenchers did not have at hand the BLB resistance-versus-pressure data. They used the ambient temperature resistance of the specimen at the quench pressure along with the atmospheric-pressure temperature coefficient to determine the specimen resistance at quench pressure and temperature. A simple calculation shows that the ratio of the resistance using the BLB data to that used by the earlier quenches goes to 1 as
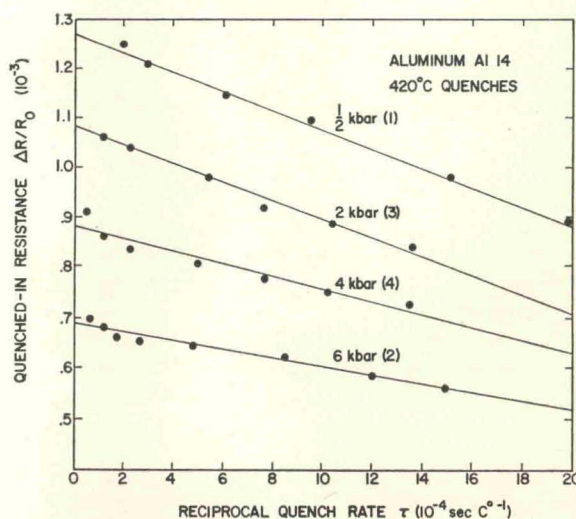

FIG. 6. Isobars of quenched-in resistance versus reciprocal quench rate for aluminum. Numbers in parentheses show sequence in which isobars were made.

P goes to zero, whereas at 10 kbar and temperatures from 600 to 700°C it may be 1.01. Thus, the earlier experimenters were quenching from 6 to 8°C too high at their 10-kbar quenches thereby cancelling part of the pressure effect. Indeed, application of this correction to the Huebener and Homan data yields a value of 6.8 cm³/mole, in remarkable agreement with the present value.

Huebener and Homan assume that a fixed quench rate will produce a fixed fractional loss of vacancies. The present results show that this is not the case. However, for their quench rates, the effect is small compared with their temperature error. Even for the 640°C quenches a measurable fraction was lost at a linear quench rate of 10^4°C sec^{-1}. Finally, the previous experimenters had to apply relatively large corrections to their data to reduce it to a fixed quench temperature. In the present experiment the precision of the temperature control eliminated the need for such corrections. It is therefore not necessary to assume a formation energy in determining ΔV_f.

The sum of the present value of ΔV_f and the earlier ΔV_m value[4] of 1.50 ± 0.15 cm³/mole is 8.3 ± 0.5 cm³/mole. This is about 80% of the molar volume. Dickerson et al.[5] find 7.2 ± 0.4 cm³/mole while Beyeler and Adda[6] report 7.3 cm³/mole. The agreement between the present value and that of Dickerson et al. is just within the limits of error. Dickerson[5] mentions considerable difficulty with chromel-alumel thermocouple deterioration during the diffusion anneals. Subsequent improvements have been made on the temperature-correction procedure used by Dickerson, but extreme care is required to keep the temperature error as small as ±5°C. Adda does not mention temperature-measurent procedure. The agreement between the present value of ΔV_f, the corrected Huebener and Homan value, and the BLB value along with the fact that ΔV_m contributes a small absolute error makes it appear that the self-diffusion values are low.

Even though the value of ΔV_{act} inferred from the quenching experiments is somewhat larger than the self-diffusion value, it is still small when compared with the values found for other fcc metals. The values for copper[6] and silver[19] are 0.91 and about 0.89 molar volumes, respectively. Theoretically, Schottky et al.[20] find 0.93, 0.97, and 0.99 molar volumes for copper, silver, and gold, respectively.

Thus, the agreement between formation, motion, and diffusion activation volumes is rather poor. Part of the discrepancy may arise from the fact that the measurements were made at three different tempera-

[19] C. T. Tomizuka, R. C. Lowell, and A. W. Lawson, Bull. Am. Phys. Soc. **5**, 181 (1960); M. Beyeler and Y. Adda, *Physics of Solids at High Pressures* (Academic Press Inc., New York, 1965), p. 349.

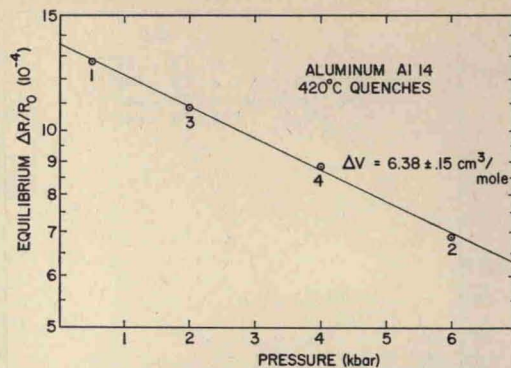[20] G. Schottky, A. Seeger, and G. Schmid, Phys. Status Solidi **4**, 419 (1964).

FIG. 7. Extrapolated relative equilibrium vacancy concentration at 420°C as a function of pressure in aluminum. Numbers by points show sequence in which points were taken on a given isotherm.

tures, so that different multiple vacancy components would be present. Part may be due to the temperature-measurement difficulties in the diffusion experiments. It would be desirable to redo the latter experiments using improved techniques.

2. Vacancy-Loss Mechanisms

Kino and Koehler[10] conclude that the temperature dependence of the fractional loss eliminates migration to grain boundaries as a possible loss mechanism. They conclude that both dislocations and impurity clusters can act as important sinks for vacancies in a quenched specimen. For the dislocation mechanism, Kino and Koehler find

$$(c_0-\bar{c})/c_0 = 0.8\pi\nu\tau_Q a^2 N_d e^{-E_m^1/kT_Q}, \qquad (4)$$

where c_0 is the equilibrium concentration at the quench temperature T_Q, $\bar{c}$ is the actual amount quenched in from T_Q at time taken to quench τ_Q, ν is the atomic vibration frequency, α is the interatomic distance, and N_d is the dislocation density. For the gold specimens used in this experiment, assuming $\nu=3\times10^{13}$ sec^{-1}, the values of N_d are 1 to 3×10^5 cm^{-2}. This value is 1 to 2 orders of magnitude smaller than observed in most quenching experiments and may reflect the fact that the specimen is not moved once it has been mounted in the vessel.

If we define Σ to be the slope of a plot of $(c_0-\bar{c})/c_0$ versus τ_Q, then differentiating (4) we find

$$\left(\frac{\partial \ln\Sigma}{\partial P}\right)_{T_Q} = \left(\frac{\partial \ln(\nu a^2 N_d)}{\partial P}\right)_{T_Q} - \frac{1}{kT_Q}\left(\frac{\partial E_m^1}{\partial P}\right)_{T_Q}. \quad (5)$$

But

$$\Delta V_m^1 = (\partial E_m^1/\partial P)_T, \qquad (6)$$

where E_m^1 is now interpreted as the Gibbs free energy of motion so that substituting (6) into (5) and re-

arranging, we see that

$$\Delta V_m{}^1 = -kT_Q\left(\frac{\partial \ln\Sigma}{\partial P}\right)_{T_Q} + kT_Q\left(\frac{\partial \ln(\nu a^2 N_d)}{\partial P}\right)_{T_Q}. \quad (7)$$

Assuming the pressure dependence of ν, a, and N_d to be small, we can interpret the pressure effect on the slopes of the loss-versus-reciprocal quench rate curves in terms of a vacancy motional volume. The value inferred from the gold data by the use of (7) turns out to be two to three times the value determined[4] from the pressure effect on the anneal of quenched-in vacancies near room temperature.

For the impurity cluster mechanism, pressure affects not only the vacancy migration rate but also r_0, the radius of the impurity nucleus. Taking the pressure derivative of the Kino and Koehler expression, we find

$$\frac{\partial \ln\Sigma}{\partial P} = \frac{\partial \ln}{\partial P}\left(\frac{\nu f(x)E_f{}^1}{a(E_m{}^1)^2}\right) + \frac{1}{r_0}\frac{\partial r_0}{\partial P} - \frac{\Delta V_m{}^1}{kT_Q}. \quad (8)$$

Although the first term may be somewhat insensitive to pressure, the radius of the nucleus will certainly be pressure-dependent, tending to decrease with increasing pressure. This term would then add to the motional volume term. Thus, unless the motional volume is temperature-dependent, the impurity cluster mechanism appears to be more compatible with these data. Further studies are being planned for specimens with larger dislocation densities and with known impurity concentrations.

Also, in agreement with the results of Kino and Koehler, we find that the fractional loss is slower than linear in τ. However, the departure from linearity does not become obvious until the quench rate is less than about 500°C sec^{-1}. At this rate, the fractional loss can no longer be considered small, as is assumed in the theory. Further studies are also being made at very slow quench rates.

B. Aluminum

1. Formation Volumes

For aluminum, there are far fewer results with which to compare. BLB have derived a single vacancy formation volume of 5.4 cm^3/mole from their thermoelectric power data and 6.0 ± 0.6 cm^3/mole from their resistance data in the 600° to 700°K range. The latter is in particularly good agreement with the present result, which was obtained at about 700°K. Buescher and Emrick[21] have recently determined ΔV_m by pressure anneals of quenched-in resistance in aluminum and have found a value of about 1.7 cm^3/mole for both single and divacancies. The sum of these two is far less than the value of 13.5 cm^3/mole found for ΔV_{act} in aluminum by Butcher, Hutto, and Ruoff[22] and of 12.9 cm^3/mole found by Beyeler and Adda.[6] These results would support the BLB conclusion that in aluminum, divacancies are the dominant defect at temperatures above 800°K where the diffusion measurements were made. It may be possible to extend the aluminum quenches to higher temperatures in order to check this conclusion although with the vessel at −80°C, temperature fluctuations increase appreciably when the specimen temperature exceeds 700°K.

2. Vacancy-Loss Mechanisms

Dislocation densities calculated for Al 14 from Eq. (1) are about 10^6 cm^{-2}, in reasonable agreement with other experiments under similar conditions. The pressure dependence of Σ for the aluminum data yields a motional volume nearly twice that determined for either single or divacancies in low-temperature pressure anneals.[21] The large error on this value, however, just includes the low-temperature value. Until further experiments are done, it can only be said that the value is more consistent with the cluster mechanism than with the dislocation mechanism.

[21] B. J. Buescher and R. M. Emrick (unpublished).
[22] B. M. Butcher, H. Hutto, and A. L. Ruoff, Appl. Phys. Letters 7, 34 (1965).